Chemical Constituents In Different Solvent Refined Coals As A Function Of The Feed Coal

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The chemical characterization of the organic constituents in solvent refined coal (SRC) is currently a subject of major concern (1) in terms of understanding present SRC processes and coal processing in general. The heterogeneous semi-solid SRC product obtained from present pilot plants represents a formidable analytical problem for identification and quantification of the organic materials present in SRC solids. Ideally, chromatographic separation of every individual organic compound present in SRC solids would allow relatively easy identification via modern analytical tools, such as, ^1H and ^{13}C Fourier transform nuclear magnetic resonance (^1H and ^{13}C FT nmr) and mass spectrometry. The feasibility of this approach, however, is questionable even assuming ideal chromatographic resolution could be achieved in light of the enormous time, quantity of material and probably weight losses accompanying each chromatographic separation. These limitations are especially acute for studies which monitor changes in organic composition as a function of a particular coal process variable (e.g., temperature, solvent, feed coal, etc.). An alternate chromatographic approach involves partial separation of the complex coal product mixture into numerous fractions based on either functionality, polarity or effective molecular size. Characterization of chromatographic fractions from this partial separation still has an obvious disadvantage in terms of analytically describing "average" molecular parameters. Although chemical characterization in terms of "average" molecular parameters is certainly a less than ideal approach, it does provide a reasonable method of monitoring processing variables provided that chromatographic fractions of a given size or type (nonpolar, polar, etc.) can be easily separated with nearly quantitative recovery. The established utility of ^1H and ^{13}C FT nmr allows a convenient method of deducing important average molecular parameters, such as, H/C aliphatic and aromatic ratios as well as assessing the relative importance of a number of other organic functional groups, (e.g., carbonyl, hydroxyl, phenol, etc.).

In the present comparison study of the organic constituents in SRC solids as a function of the SRC processing feed coal, we have employed gel permeation chromatography (2,3) for separation of the SRC solids into fractions based on effective molecular size rather than organic functionality or polarity. This approach has the advantage of providing "sized" preparative fractions (0.5-2.0 grams) with nearly quantitative recovery of the injected material from the chromatographic column.

Relatively large quantities of material were necessary for measuring metal content via flameless atomic absorption and for determining the nature and concentration of the organic constituents via ^1H and ^{13}C FT nmr techniques (4) in conjunction with elemental combustion and average molecular weight (vapor phase osmometry) data. The five SRC samples derived from different feed coals were obtained from a pilot plant operating at Wilsonville, Alabama. The SRC samples were obtained from eastern feed coals (Pittsburgh #8, and Western Kentucky #9 & #14), Illinois feed coals (Illinois #6 and Monterey), and a western coal (Amax). Preparative separation of the tetrahydrofuran (THF) soluble portion of each SRC sample provided four fractions using Bio-Beads S-X4 as the column packing. The elution volumes were held constant for each chromatographic fraction collected regardless of the SRC sample employed. The weight percent distribution for fractions 10 through 40 which correspond to decreasing effective molecular size along with the THF insoluble fraction (-10) are presented in Table 1. As indicated by the data in Table 1, all the SRC samples are greater than 88% soluble in THF. Although considerable weight changes occur as a function of the SRC feed coal sample between

Table I

Analytical Data For Molecular "Sized" Fractions of Various Solvent Refined Coals*

FRACTION #	PITTSBURGH #8	AMAX	W. KENTUCKY #9 & #14	ILLINOIS #6	MONTEREY
10	19.2[a] (711)[0.82]	23.6[a] (959)[0.79]	28.4[a] (795)[0.81]	39.2[a] (611)[0.83]	33.9[a] (652)[0.85]
20	24.1 (487)[0.92]	16.4 (597)[0.85]	17.1 (408)[0.91]	20.0 (447)[0.88]	22.8 (556)[0.80]
30	47.9 (388)[0.93]	48.6 (547)[0.76]	38.3 (313)[0.90]	30.4 (385)[0.85]	40.7 (479) 0.89]
40	5.9	3.2	4.7	1.6	2.6
-10**	2.9 [0.70]	8.2 [0.62]	11.6 [0.72]	8.8 [0.73]	0

* Average molecular weight data in parenthesis via vapor phase osmometry. Hydrogen to carbon (H/C) total ratio data in brackets.

** THF insoluble fraction, percent solubility determined by suspending 1 gram of the SRC sample in 200 ml of THF and stirring for 3 hours. The resulting solution was filtered through a millipore filter (LWSP) and the residue was dried before weighing.

[a]Fractional weight percentage

fractions 10 and 30, the molecular weight data are relatively consistent for a given fraction. Some variations do, however, occur for the Amax and Monterey SRC samples.

In characterizing the organic constituents for the major soluble fractions, a cursory difference between the eastern coals (e.g., Pittsburgh #8 and W. Kentucky #9 & #14) with the western coal (Amax) is evident. The total hydrogen to carbon ratio (H/C) data obtained from elemental combustion are tabulated in Table 1 with the Amax SRC fractions consistently exhibiting the lowest (H/C) ratios for each fraction. The relatively constant nature of the SRC samples derived from the eastern and Illinois #6 feed coals is indicated by the relatively narrow range of average molecular formulas presented in Table 2. The Amax and Monterey SRC fractions are exceptions in this regard (Table 3) and have consistently larger molecular formulas for a given fraction as previously suggested by the molecular weight data in Table 1.

Table 2

Range of Average Molecular Formulas for Western Kentucky #9 & 14
Pittsburgh #8 and Illinois #6 SRC Fractions *

FRACTION	FORMULA
10	$C_{41-55}H_{35-45}O_{3.7-4.7}S_{0.2-0.4}N_{0.7-1.0}$
20	$C_{27-33}H_{24-30}O_{2.5-3.4}S_{0.2-0.4}N_{0.5-0.6}$
30	$C_{22-27}H_{20-24}O_{1.4-2.2}S_{0.1-0.2}N_{0.4}$

*Values based on average molecular weights and elemental combustion data

Table 3

Average Molecular Formulas For Amax and Monterey SRC Fractions

FUNCTION	MONTEREY	AMAX
10	$C_{43.4}H_{37.0}O_{4.5}$ $S_{0.3}N_{0.8}$	$C_{67.5}H_{52.7}O_{4.3}$ $S_{0.4}N_{1.0}$
20	$C_{38.0}H_{30.3}O_{2.6}$ $S_{0.6}N_{0.7}$	$C_{40.0}H_{34.0}O_{4.1}$ $S_{0.3}N_{0.6}$
30	$C_{34.2}H_{30.9}O_{1.5}$ $S_{0.2}N_{0.5}$	$C_{37.8}H_{34.0}O_{3.0}$ $S_{0.1}N_{0.5}$

*Values based on average molecular weight and elemental combustion data

The ^{1}H and ^{13}C nmr spectra superficially appear very similar for a given SRC fraction regardless of the feed coal. Typical ^{13}C and ^{1}H FT nmr spectra for Amax Fraction 30 are presented in Figures 1 and 2, respectively. Quantitative nmr measurements, however, indicate major changes do occur in the aliphatic and aromatic (H/C) ratios as summarized for fraction 30 samples in Table 4. The unusually low aliphatic (H/C) ratio for the Amax sample is very suggestive of highly condensed cyclic aliphatic networks (e.g., substituted adamantanes) previously suggested by a Mobile group (5).

Further trends and comparisons of the organic constituents will be the major thrust of this presentation with particular attention focusing on the Amax sample.

Table 4

(H/C) Aromatic and Aliphatic Ratios
For SRC Fraction 30 Samples*

SRC	$(H/C)_{ALP.}$	$(H/C)_{ARO}$	F_A(Aromaticity)
Pittsburgh #8	1.66	0.49	0.64
West. Kentucky #9 & #14	2.09	0.44	0.71
Illinois #6	1.35	0.57	0.64
Monterey	2.12	0.46	0.73
Amax	1.15	0.50	0.63

* Values obtained from quantitative ^{1}H and ^{13}C FT nmr measurements.

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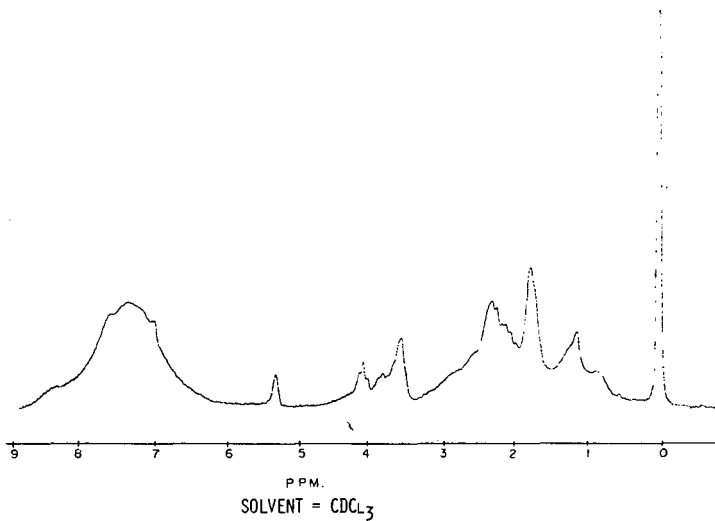
FIGURE 1

^{1}H Spectrum of Amax Fraction 30
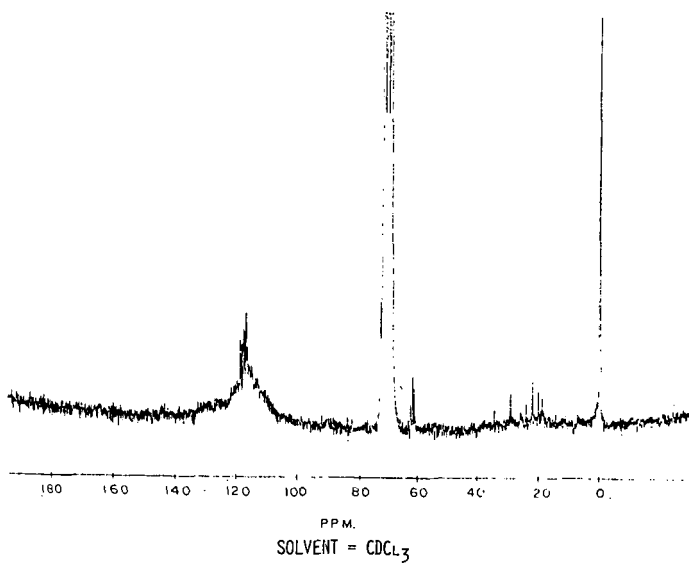
PPM.

SOLVENT = CDCL₃

FIGURE 2

^{13}C Spectrum of Amax Fraction 30

PPM.

SOLVENT = CDCL₃

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FIGURE 1

^{1}H Spectrum of Amax Fraction 30

PPM.

SOLVENT = CDCL$_3$

FIGURE 2

^{13}C Spectrum of Amax Fraction 30

PPM.

SOLVENT = CDCL$_3$

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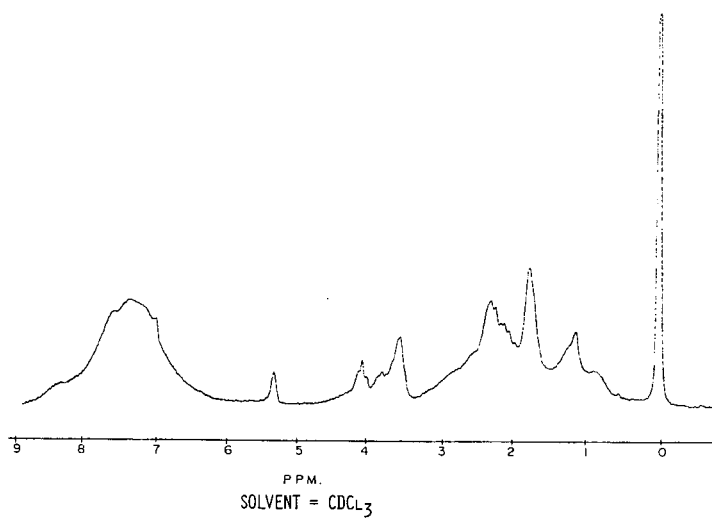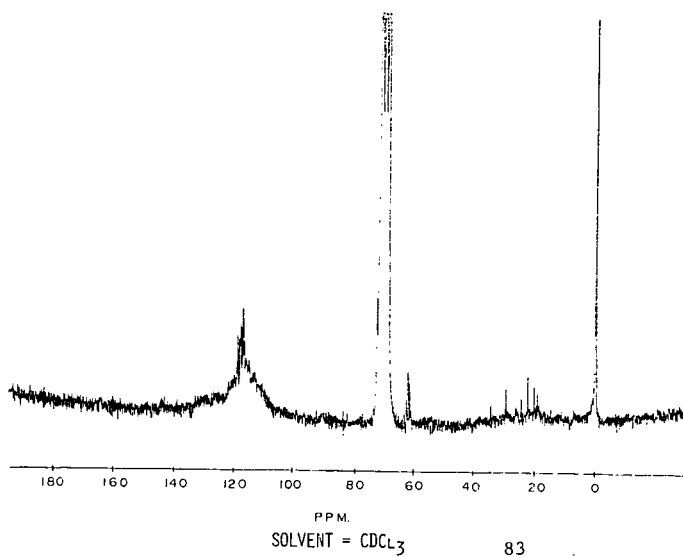
COMPARISON OF SOLVENT REFINED LIGNITES WITH SOLVENT REFINED BITU-
MINOUS COALS.

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Comparison of SRL and SRC

Introduction
     A considerable amount of work is currently being conducted on solvent refining
of bituminous coals. The resulting solvent refined coal (SRC) can be used as a boil-
er fuel or as a feedstock for further refining. A parallel program on lignite coal is
being carried out in our Chemical Engineering Department (Project Lignite). Con-
sidering the properties of the starting coals, it was initially assumed that SRC and
solvent refined lignite (SRL) would be greatly different and, thus, second stage re-
fining reactions and conditions would have to be developed and "fine tuned" for the
different feedstocks. As these programs developed, however, it soon became appar-
ant that SRL and SRC were more similar to each other than the starting coals were.
In view of these similarities and because of a lack of definitive evidence to the con-
trary, it has been generally accepted that the second stage reactions and conditions
can be simultaneously, rather than separately developed.
     In view of the importance of this tentative conclusion to our work, we have set
about examining the similarities and differences between a wide variety of SRL and
SRC samples. Our preliminary results (1) were consistent with the conclusion that
SRC and SRL were nearly the same within the limits of the experiments and samples
we were using. We have now obtained more representative samples of both SRL and
SRC produced under more commercial conditions and report their comparison here.
     Procedure: Samples refined from lignite, sub bituminous and bituminous coals
were obtained. (2,3) In addition, as controls, more deeply hydrogenated samples
from a COSteam process and from second stage hydrogenation of SRL were included
in the comparison.(3) The method of analysis was similar to that used previously
(1) using the whole coal samples. Ultimate analyses, including neutron activation
oxygen analysis, nonaqueous titrations, uv, mw, nmr and esr spectroscopy were used
to examine these samples. A difficulty rapidly developed. Several of the samples
contained unreacted coal and ash. Initially we thought a comparison could be made by
correcting for these insoluble materials on the basis of pyridine solubility of the sam-
ple. Neutron activation (naa) oxygen analysis showed, however, that oxygen by differ-
ence and by naa for maf samples were fairly close, but samples containing ash de-
viated considerably (Table 1). Thus, the variability of oxygen in the ash and unreacted
coal led to large errors in the amount of oxygen in the maf material. Because the
oxygen content could be critical to a lignite-bituminous coal comparison, we set out
to develop an exact, reproducible laboratory deashing procedure. The deashing pro-
cedure was based on pyridine Soxhlet extraction, filtration of the eluate and removal
of pyridine under standard conditions. The amount of pyridine remaining in each sam-
ple was checked by pmr. Several samples were crosschecked by mass spectroscopy.
As little as 0. 2% pyridine could have been detected. None was found. Table I shows
the percentage of each sample found soluble in pyridine with and without 5 μ filtration.
The results show the 5 μ sizing procedure seems desirable, especially in view of
the variable amounts of materials obtained from different samples by this technique.
For laboratory studies we would like to propose this separatory technique as a stand-
ard procedure to define an SRC or SRL (cf Experimental Section).

Discussion of Analytical - Spectroscopic Results.

     A. NMR: Proton nmr analysis of samples before and after deashing indicates
no gross changes in the samples. Nevertheless, small systematic changes did oc-
cur. Samples, both SRL and SRC, initially containing ash and unreacted coal had
the same $H_{ar}/(H\alpha + H_o)$ ratio within experimental error before and after deashing.

(Table II). Maf samples showed changes of 0.07-0.26 in this ratio, which is outside the precision of the measurements. Another subtle, but consistent trend for nearly all samples was a decrease in the $H\alpha/H_O$ ratio on deashing. This was true for initially maf, as well as samples with ash and unreacted coal. Furthermore, this change in ratio was 0.-0.48 for SRL's and larger, 0.36-1.27, for SRC's. Excluding the Amax sample, the range was 1.17-1.27. The $H\alpha/H_O$ decreased by 0.83-1.17 for two samples when the pyridine insoluble fraction was simply filtered off (nmr s were run with all insoluble material present in non maf material).

Only experience will show if the change in $H\alpha/H_O$ ratio, caused by laboratory deashing, can be used to identify the coal used for SRC or SRL preparation. whether these small changes are caused by material in the ash or by chemical reaction during the deashing process also remains to be investigated. Our experience with FT carbon-13 determined C_{ar}/C total (ie fa) ratios are consistent with a recent report (4) that the ratios determined from proton and carbon-13 nmr are very similar. (eg. for M11A Carbon-13 = 0.815+0.009 and from proton fa=0.813).

B. <u>Molecular Weight</u>: The molecular weights (by VPO) of the samples before and after deashing were also measured. The precision on the single determinations before deashing is much less than for the three concentration extrapolated values determined on the laboratory deashed material. Even so, the two values for each sample were either the same within experimental error or very close to each other (with the exception of Tacoma (maf), which increased significantly). The ranges, in general, both before and after deashing are not grossly different, although the SRC's (before 420-597; after 460-620) are marginally higher in mw than the SRL's (before 400-598; after 428-481).

C. <u>Ultraviolet Spectra</u>: The ultraviolet spectra for these samples was run between 270-400 nm and is plotted vs $E1\%$ in Fig. 1. These and other such samples have remarkably featureless spectra. All samples thus far examined, fall generally within the range shown. These factors make it unlikely that SRL's and SRC's may be distinguished by such data. Comparison to the COSteam and J-1-11-87 samples, indicates that larger reductive changes, however, can be characterized by uv spectra (Fig. 1). There also seems to be a relationship between the integrated uv absorption and both Har and Halip from nmr data (Fig. 2).

D. <u>Acid base properties</u>: non aqueous titration for acidity gave a range of 1.34-2.80 meq/g for SRL's and 1.45-2.95 for SRC's. The basic titer ranged for SRL's 0.30-0.63, and 0.52-0.84 meq/g for SRC's. Where comparisons can currently be made, the oxygen content is marginally lower for SRL's (despite the fact that initially it was much higher in lignite) than for SRC's. Nitrogen content for SRL's is generally lower than for SRC's. Thus, the acidity and basicity of both SRL's and SRC's seem to parallel roughly the percentage oxygen and nitrogen respectively in the sample.

The percentages of C, H are typical (Amax %C is low and is being checked) of other samples with carbon ranging 85-90% (maf) and hydrogen, 5-6% for SRL and SRC samples. The sulfur content ranges somewhat higher for SRC's, 1.30-3.68% (but only a trace for Amax) than for SRL's, 0.85-1.24; probably a reflection of the sulfur content of starting coal.

E. <u>Electron spin resonance</u>: The esr spectra of the samples was measured, with the results given in Table II. The range of g-values was very small for all samples investigated, 2.0026-2.0028. The g values are in good agreement with those reported for coals having carbon contents over 80%. The linewidths for SRL's ranged 3.8-4.8 gauss; for SRC's 1.7 to 7.6. The linewidth appears marginally lower than that expected for a vitrain of comparable hydrogen content. (5)

<u>Summary of Analytical Comparisons</u>: While the comparisons are not yet complete, the gross makeup of the samples indicate that SRL's and SRC's are quite similar. The variations noted in the uv, molecular weight, esr, and nmr analyses may be more a function of reaction conditions than of starting coal. The precentage composition and acid-base characteristics seem to indicate that the starting coal properties, particularly nitrogen, sulfur and oxygen percentages, may be carried over into the solvent refined products, although they are affected also, to a large extent, by reaction conditions.

Furthermore, in cases which we have investigated thus far, hydrotreating of

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SRL and SRC have shown similar trends, in that their reactivities and product distributions depend more on how they are made, stored and treated than on the starting coal.

Assessment of Analytical Procedures: Several difficulties have emerged in these analyses for whole solvent refined samples. A standardized laboratory deashing procedure which we have developed, appears necessary. Oxygen analysis on maf samples by difference may be generally acceptable, but should be checked with neutron activation analysis and is absolutely essential with samples containing unreacted coal and ash. A standardized procedure which we are developing needs to be uniformly applied to pulsed carbon-13 nmr analyses.

Future Work in Analysis of Gross Solvent Refined Coal Samples: Application of Carbon-13 nmr techniques have been applied to coal derived samples, but generally only to that portion of the sample soluble in a "desirable" nmr solvent (CS_2, $CDCl_3$, etc.). Whole solvent refined samples containing large amounts of preasphaltenes (like SRL and SRC) are not soluble in these solvents. In order to properly characterize whole samples, either new solvents or new techniques have to be developed. We are working on both.

A second area of critical concern to us is the qualitative way comparisons currently must be made. A critical set of standardized measurements needs to be developed (which we have alluded to above). These measurements should then be reduced to a set of critical structural factors, probably through a computerized technique which will allow direct quantitative comparison of samples. While inroads are being made on this approach, (6) better methods need to be developed.

Experimental Section

Analyses were performed by Midwest Micro and Spang Laboratories. Nmr spectra were measured on an EM-390 and analyzed, as previously described. (1) Titrations were conducted, as previously indicated. (1)

Neutron activated analysis was carried out by Intelcom Rad Tech, San Diego, CA. Uv spectra were measured on a Cary 14 in dimethyl acetamide. Esr were determined on a Bruker ER 420. Molecular weights were measured by Spang, and with a Corona Wescan 232 VPO in dimethyl formamide, the latter at 74.8^O at three different concentrations with extrapolation to infinite dilution. Very little association was noted in this solvent.

Laboratory Deashing Procedure: A Whatman no. 1 Soxhlet thimble was shrunk in acetone, dried at $110^O C$, cooled in a dessicator and weighed to constant weight. A 3 to 5 g sample of SRL or SRC was weighed into the thimble and extracted with pyridine for 24 hrs under nitrogen. The thimble was dried at 110° for 24 hrs, cooled in a dessicator and weighed. The pyridine solution was filtered through a preweighed 5 μ Teflon filter. The sum of the sample in the thimble and on the filter constituted the undissolved sample by definition. Most of the pyridine in the filtrate was removed at 50° (1mm), then at 50° (0.05mm) for 24 hrs. The sample was scraped into a drying boat and further dried at 56° (0.1mm) for 24 hrs. After grinding in a mortar, the sample was redried at 100° (0.1mm) for 24 hrs more. Less than 1% of pyridine could be observed by nmr in hexamethyl phosphoramide. Mass spectrometry indicated less than 0.2% pyridine in several samples.

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Table I

Comparison of Deashing Techniques

Sample	Simple Extraction	Filtration Extraction	% O by difference	by NAA**
M11-A*	100	96.8	5.80	2.35
Tacoma II*	99.7	95.4	3.81	3.22
Amax*	99.8	94.1	12.36	3.37
M5-C	80.1	84.2	3.88	7.31
M13-A	86.1	77.6	2.91	5.37
M21-A	75.8	68.0	7.04	5.57
Tacoma I	71.8	69.6	10.7	6.53
Wilsonville	76.4	59.3	8.49	7.71

* maf as received
** neutron activation analysis

Table II

	M11-A	Amax	Tacoma (maf)
%C	89.31	80.57	87.19
%H	5.80	5.50	5.45
%N	1.11	1.57	2.25
%S	0.86	< 0.02	1.3
%O(NA)	2.35	3.37	3.22
MW	497+9	585+7	624+19
Acid meq/mole	2.22	2.95	3.35
Base meq/mole	0.30	0.55	0.84
Pyr. sol. (%)	96.80	94.10	95.38
Har/Hα+Ho	1.07	1.00	0.826
Hα/Ho	2.58	2.22	3.46
fa	0.813	0.797	0.897
σ	0.304	0.399	0.397
Haru/Car	0.707	0.849	0.701
Cl	1.39	1.45	1.29
Ra	5.28	3.41	5.82
Esr ΔH(pp)(G)	4.8		7.6
g value	2.0026		2.0028

Molecular Formula

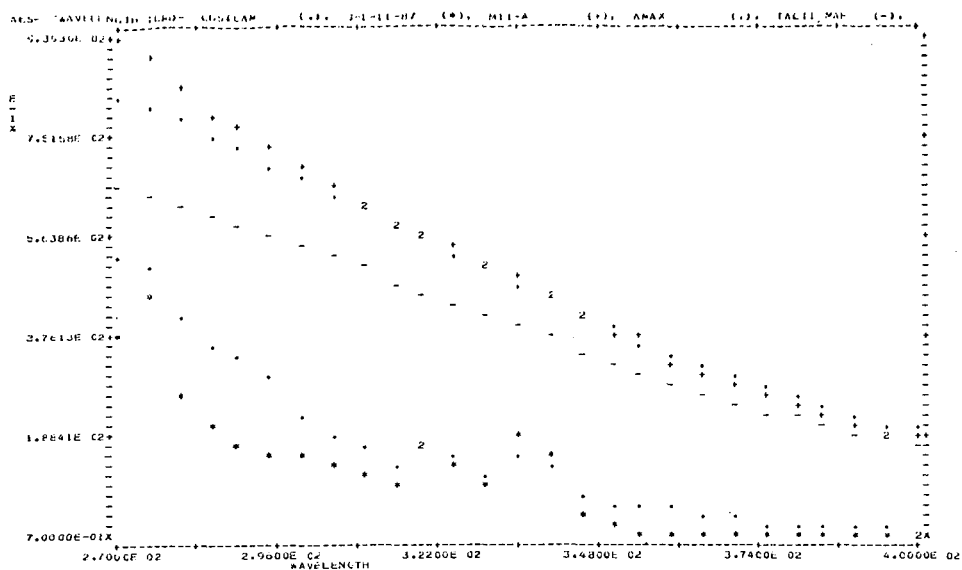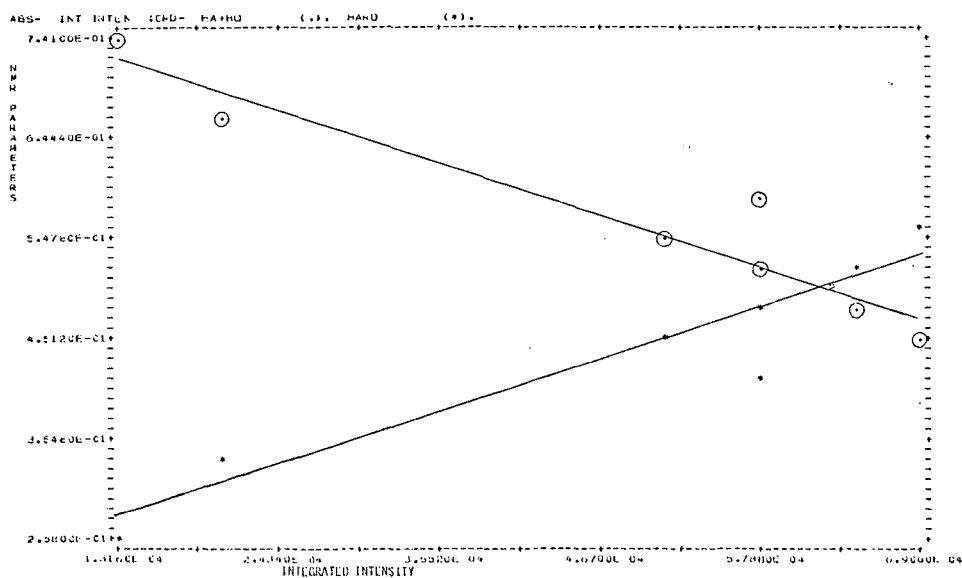|	M11-A	Amax	Tacoma (maf)
C	36.9	39.2	45.3
H	28.8	32.1	34.0
N	0.39	0.66	1.00
S	0.13	——	0.25
O	0.73	1.22	1.26
Acid eq/mole	1.10	1.72	2.09
Base eq/mole	0.15	0.32	0.52

FIGURE 1

FIGURE 2

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References

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2. Samples were generously supplied by Project Lignite, University of North Dakota and the Grand Forks Energy Research Center.

3. Samples are designated as follows:
   M5-C-(undeashed) Conditions: 2500 psi of 1:1 CO:H_2 at 455°C (max).[*]

   M11-A-(deashed) Conditions: 2500 psi of 1:1 CO:H_2 at 479°C (max).[*]

   M13-A-(partly deashed) Conditions: 2500 psi of 1:1 CO:H_2 at 453°C (max).[*]
   M21-A- (undeashed) Conditions: 2000 psi of 1:3 CO:H_2 at 439°C (max).[*]
   Tacoma I (undeashed): Pittsburgh and Midway Coal Co., Merriam, Kansas (a Gulf subsidiary). From a Kentucky no. 9 and no. 14 blend of bituminous coal from the Colonial Mine. Conditions: PDU, continuous flow, 1500 psi of H_2 (85% min), 450°C (max), using recycle solvent; product not filtered and stored in the open.
   Tacoma II (deashed): Same as Tacoma I except product filtered before solvent distilled. (maf)
   Amax-Southern Services, Inc., Burmingham, Alabama (an ERPI contractor). From a sub-bituminous coal from the Bel Air Mine in Wyoming. Conditions: continuous flow, 2500 psi of H_2 and recycle gases, 460° (max) using recycle heavy in phenols with 1, 2 and 3 ring aromatics.
   Wilsonville-Prepared essentially by the procedure for Amax.
   J-1-11-87: Reduction fraction of KC-SRL. Conditions: batch autoclave, 4500 psi (max) of H_2 at 450° for 2 hrs. using presulfided HT-100 (NiMo) catalyst b.p. 110-180°C (0.4 mm) followed by removal of solid which precipitated on standing in the freezer for ca. month.
   COSteam: Pittsburgh Energy Research Laboratory (an ERDA Lab). N. D. Lignite treated in a tubular reactor with synthesis gas under COSteam conditions. Conditions: continuous flow, 4000 psi of CO:H_2. Whole product chromatographed on alumina. This fraction eluted with toluene (aromatics fraction). 126-2 (Separation done in Grand Forks Energy Research Laboratory)

4. H. L. Retcofsky, F. K. Schweighardt and M. Hough, Analytical Chem., 49 (4), 585 (1977).

5. H. L. Retcofsky, G. P. Thompson, R. Raymond and R. A. Friedel, Fuel 54, 126 (1975) and papers cited therein.

6. M. Oka, H.-C. Chung and G. R. Gavalas, ibid, 56, 3 (1977).

[*] Solvent refined N.D. lignite by Project Lignite of the University of North Dakota. PDU operation, FS-120 as make up solvent during recycle operation using ca. 1.8:1 solvent to coal.

ELECTRON SPIN RESONANCE STUDIES OF COALS AND COAL-DERIVED ASPHALTENES

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INTRODUCTION

The discovery of electron spin resonance (esr) absorption in natural carbons by Uebersfeld (1) and Ingram (2) prompted a number of investigators to apply the technique to coal and materials derived from coal. At least three excellent review articles describing the early esr studies of coals have been published (3-5). Although the exact nature of the species responsible for the esr absorption has not been established unambiguously, it is generally thought that the unpaired electrons, at least in non-anthracitic and possibly young anthracitic coals, are associated with organic free radical structures. One group of investigators, however, has proposed that charge-transfer complexes rather than stable free radicals may be responsible for the absorption (6).

During the present investigation, esr spectra were obtained for vitrains and fusains from a large number of coals. For most ranks of coal, samples of both lithotypes were studied. The objectives of the investigation were:. 1) to better characterize the immediate chemical environment of the unpaired electrons; 2) to deduce information about the metamorphic changes that occur during vitrinization and fusinization; and 3) to provide needed background information for future studies of the role of free radicals in coal liquefaction. To further pursue the latter objective, esr spectra of asphaltenes, which are considered by many coal researchers to be intermediates in the conversion of coal to liquid fuels, were also obtained. A secondary purpose for examining the asphaltenes was to explore the recent hypothesis (7) that charge-transfer interactions may be important binding forces between the acid/neutral and base components in these materials.

EXPERIMENTAL

Samples. Most of the vitrains and fusains studied were of high petrographic purity, although several of the vitrains are more appropriately described as vitrain-rich samples. Sixty-three vitrains, including samples from Antarctica, Austria, Canada, Germany, Japan, Pakistan, Peru, the United States, and Yugoslavia, and 30 fusains, most of which were separated from U. S. coals, were investigated. Petrographic characterization and other properties of many of these samples were published previously (8).

The asphaltene samples were derived from products from the Pittsburgh Energy Research Center's SYNTHOIL (9) coal liquefaction Process Development Unit using a recently described solvent separation method (10). The acid/neutral and base components of the asphaltenes were prepared according to published procedures (11).

Spectral Measurements. The esr measurements were made over a period of approximately ten years. The experimental techniques were essentially those published earlier (12) except for minor modifications that were made over the years to facilitate the measurements. All esr measurements were made on evacuated samples ($\sim 10^{-6}$ torr) to prevent line broadening by oxygen in the air. The electrical properties of many of the higher rank samples necessitated that the samples be dispersed in a non-conducting medium to avoid microwave skin effects.

RESULTS AND DISCUSSION

Vitrains and Fusains. ESR data obtained for vitrains and fusains during the present investigation are far too numerous to tabulate here; complete listings of the data are available from the authors upon request. The plots of Figures 1-6 show some of the more significant correlations of the data with coal composition or coal rank.

The concentrations of unpaired electrons in the vitrains, as estimated by comparing the esr intensity of each sample with that of a standard sample of diphenylpicrylhydrazyl, are shown as a function of the carbon contents of the samples in Figure 1. The relationship of Figure 1 is similar to those from earlier studies (3-5, 12), although the scatter of the data points is more pronounced in the present work. These data show that, in general, the concentrations of unpaired electrons increase with increasing coal rank up to a carbon content of approximately 94% after which the spin concentrations decrease rapidly. The initial, crudely exponential increase in spin concentration is generally attributed to the formation of organic free radicals during vitrinization. The free radical electrons are thought to be delocalized over aromatic rings and thus stabilized by resonance. Resonance stabilization of the radicals is greater for the vitrains from higher rank coals since these presumably contain the larger polynuclear condensed aromatic ring systems. The precipitous decrease in spin concentration above 94% C results from the increased conductivity of the samples.

In contrast to the results for vitrains, the spin concentrations of the fusains (Figure 2) exhibit no readily discernable dependence on carbon content. The wide variation in thermal history experienced by fusains during their formation is the most likely explanation for this behavior (13).

The changes that occur in esr linewidths and g values during vitrinization and fusinization are shown in Figures 3-6. The abscissa used in these figures is based on the coalification plots of Schopf (14) with slight modifications by Parks (15) and the present authors. The ranks shown on the plots are those of the parent coals as determined by standard procedures (16).

For the vitrains, an increase in esr linewidth with increasing rank is first observed (Figure 3); this trend is reversed at the low rank bituminous stage. The rate of decrease becomes larger as coalification progresses through the higher rank bituminous stages to the early anthracitic stages. Some of the anthracites and most of the meta-anthracites exhibit very broad lines (not shown in the figure); a linewidth in excess of 60 gauss was observed for one such coal. The linewidth results can be interpreted as follows: Nuclear broadening, i.e., unresolved proton-electron hyperfine interactions, plays an important role in the observed linewidths of peats, lignites, and bituminous coals. The relatively narrow lines observed in the spectra of some of the anthracites probably result from the smaller number of protons in the samples, although exchange narrowing of the esr resonances may also be occurring. The proton line broadening hypothesis is supported by a recent esr study of coals before and after catalytic dehydrogenation (17). The very large linewidths of the highest rank materials are undoubtedly due to the presence of graphite-like structures which form during the latter stages of coalification. The difficulty in differentiating between anthracites and meta-anthracites (18) may be responsible for the apparent lack of predictability of linewidths in vitrains from coals of these ranks.

The esr linewidths for the fusains (Figure 4) are very small, frequently less than one gauss, except for samples from the lowest rank coals. Unlike the results for the vitrains, no evidence was found for the formation of graphitic structures during the latter stages of fusinization. In addition, the gradual decrease in

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linewidths of vitrains as coalification proceeds from the low rank bituminous stages
to the early anthracitic stages (Figure 3) appears as a very rapid change in the
fusinization plot (Figure 4). This is in accord with Schopf's (14) representation
of fusinization as a process which has an early inception and progresses rapidly in
the peat and lignitic stages, after which the metamorphic changes become nearly
imperceptible. Vitrinization, on the other hand, involves a progressive change
throughout all stages of rank development.

The relationship between the g values of the lithotypes and coal rank (Figures 5 and
6) also supports Schopf's theories of vitrinization and fusinization. The large g
values found for the vitrains from meta-anthracites is in accord with the final step
in vitrinization being the fusing of aromatic rings into graphite-like structures.
The g value of each of the vitrains and fusains is higher than that of the free
electron and lies in the spectral region expected for simple organic free radicals.
The only exceptions are vitrains from the more highly metamorphized coals, one of
which exhibited a g value of 2.011.

The fact that esr g values of organic free radicals are greatest for radicals in
which the unpaired electron is localized or partially localized on atoms having high
spin-orbit coupling constants can be used to explain the g value results for vi-
trains. Since the heteroatom contents of coals decrease with increasing rank, the
high g values for peats and lignites can be interpreted in terms of aromatic radi-
cals with some partial localization of the unpaired electrons on heteroatoms, par-
ticularly but not exclusively oxygen. As coalification progresses the g values
decrease, suggesting that the radicals become more "hydrocarbon-like." The g values
of many of the vitrains from bituminous and young anthracitic coals compare favor-
ably with those exhibited by aromatic hydrocarbon radicals. During the final stages
of coalification, the g values become quite large as one would expect if continued
condensation of the aromatic rings into graphite structures occurs. The observation
of a small, but reproducible, anisotropy in the g value of certain anthracites (Fig-
ure 7) suggests that some ordering of the polynuclear condensed aromatic rings is
occurring.

Coal-Derived Asphaltenes. To better understand the chemistry of coal liquefaction,
an esr investigation of coal-derived asphaltenes was initiated. Preliminary results
are presented here. Of particular concern was the temperature variation of the esr
intensities of asphaltenes and their acid/neutral and base components (Figure 8).
The most significant finding to date is that the weighted average of the temperature
dependencies of the two components reproduces the temperature dependence of the
total asphaltene (before separation) exceptionally well. This suggests that charge
transfer interactions, at least in the Mullikan sense, are relatively unimportant
binding forces between the acid/neutral and base components of the asphaltenes.

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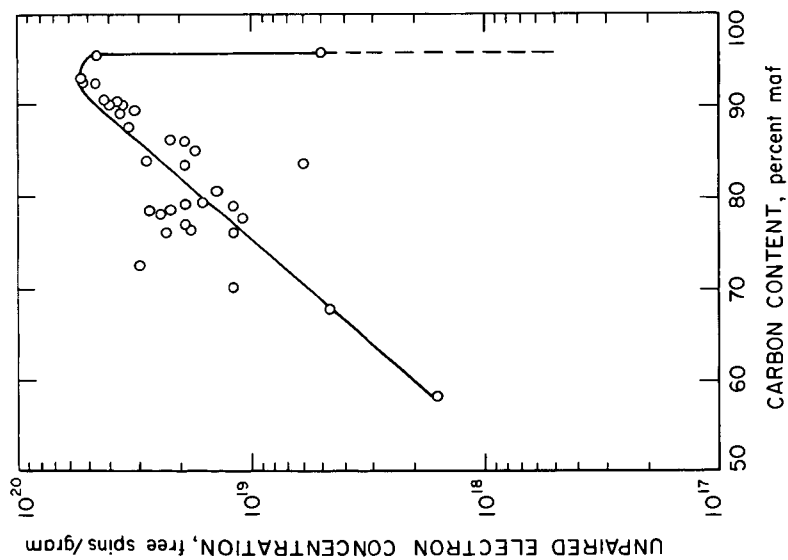18. M. Mentser, H. J. O'Donnell, and S. Ergun, Fuel, 41, 153 (1962).

Figure 1—Concentrations of unpaired electrons as a function of carbon content for vitrains from selected coals.
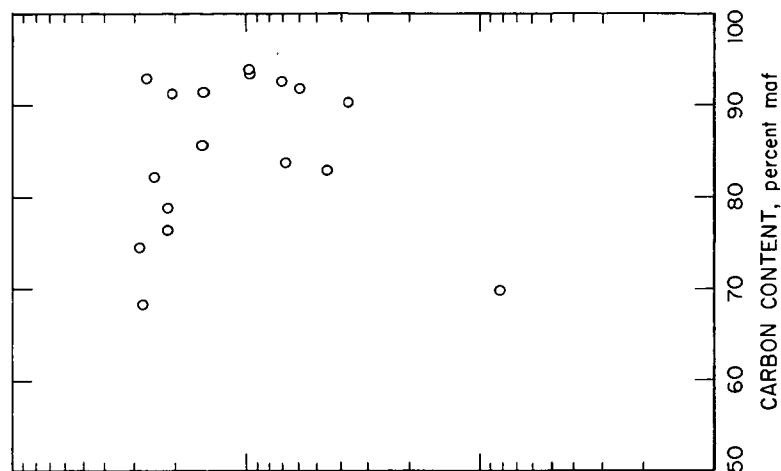
Figure 2—Concentrations of unpaired electrons as a function of carbon content for fusains from selected coals.

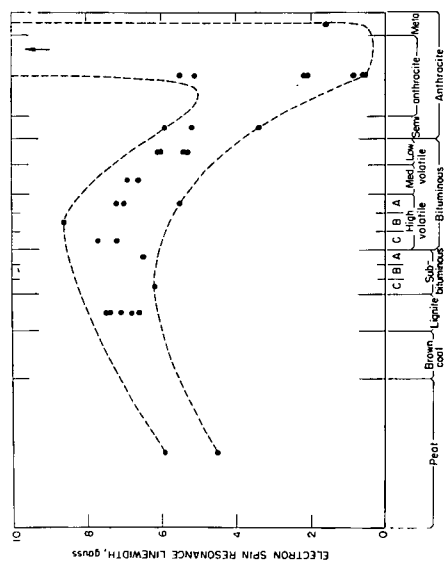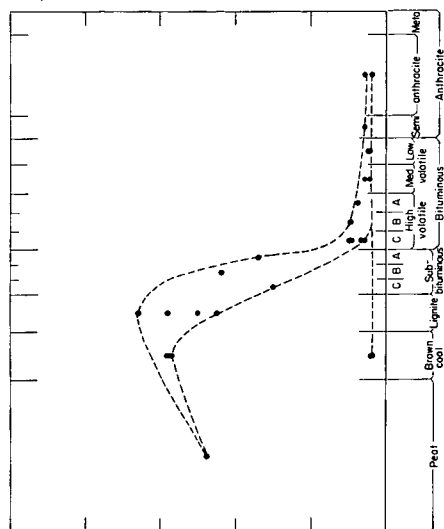Figure 4—Electron spin resonance linewidths as a function of coal rank for fusains from selected coals.

Figure 3—Electron spin resonance linewidths as a function of coal rank for vitrains from selected coals.

ELECTRON SPIN RESONANCE LINEWIDTH, gauss
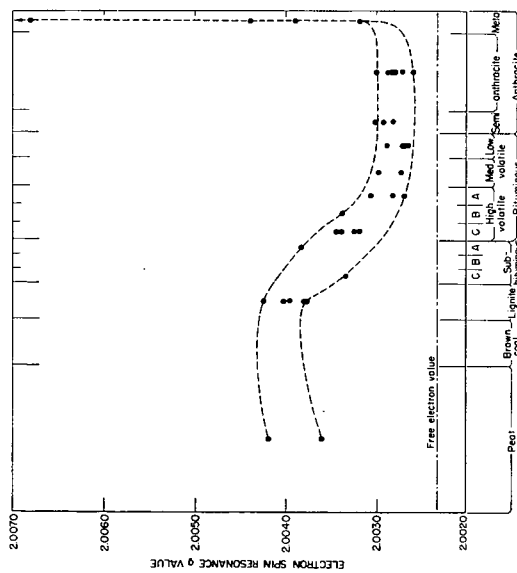
Figure 5—Electron spin resonance g values as a function of coal rank for vitrains from selected coals
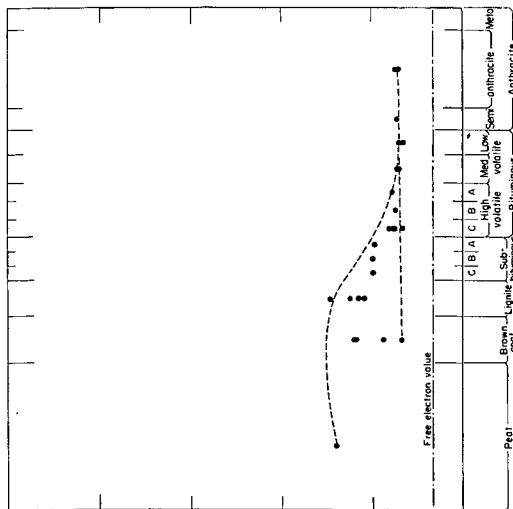
Figure 6—Electron spin resonance g values as a function of coal rank for fusains from selected coals

ELECTRON SPIN RESONANCE g VALUE

2.0070 2.0060 2.0050 2.0040 2.0030 2.0020

Free electron value

Peat — Brown coal — Lignite — Sub-bituminous (C B A) — Bituminous (High volatile C B A / Med / Low volatile) — Anthracite (Semi-anthracite / Anthracite / Meta)

Figure 7 – g Value anisotropy in Huber Mine anthracite

Figure 8 – Variable temperature ESR data for asphaltenes and components.

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ISOTOPIC STUDIES OF THERMALLY INDUCED REACTIONS OF

COAL AND COAL-LIKE STRUCTURES

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Paul H. Maupin, and W. H. Roark[1]

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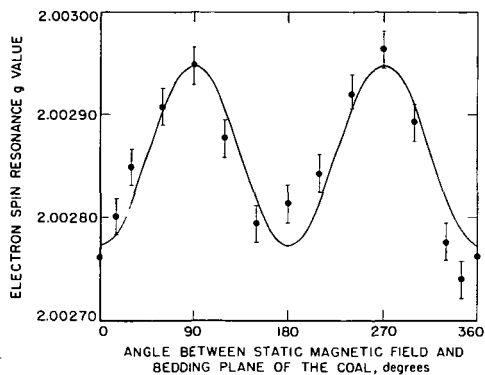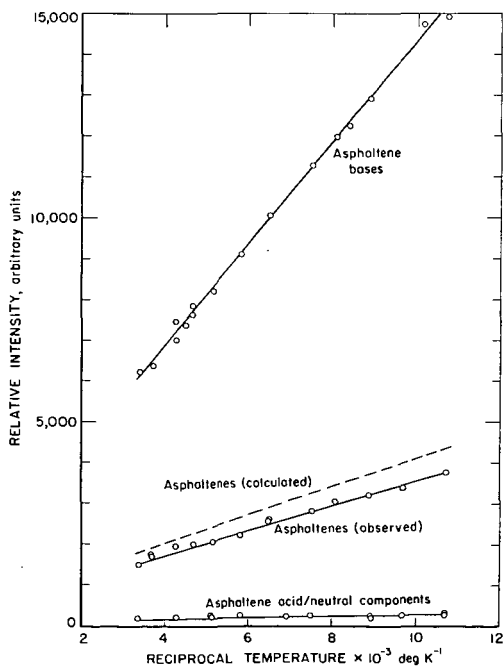We recently [2] reported that under conditions of coal conversion (tetralin, 400°) several diarylalkanes undergo carbon-carbon cleavage, and that the scission of carbon-carbon bonds must therefore be considered as an important process in asphaltene formation. We also reported [2] that vitrinite (from Illinois No. 6 coal) was a "better hydrogen transfer agent" than tetralin itself for the hydrogenolysis of 1,1,2-triphenylethane to diphenylmethane and toluene. We have now extended these studies to establish a) that vitrinite is indeed a better hydrogen donor than tetralin toward several organic structures; b) that tetralin, in addition to its function as a hydrogen donor, can undergo certain other reactions with coal and with coal-like structures which involve both carbon-carbon bond formation and bond cleavage.

A Comparison of Tetralin and Vitrinite as H-Donors

When 1,2-diphenyl-1-p-tolylethane is heated at 400° (either in glass capillaries or in stainless steel tubes) with an excess of tetralin, the major products are toluene and phenyl-p-tolylmethane. The same products are obtained when 1,2-diphenyl-1-p-tolylethane is heated at 400° in the presence of an excess of vitrinite (handpicked from Illinois No. 6 coal). Given in Table I is a comparison of the

Table I

A Comparison of Tetralin and Illinois

No. 6 Vitrinite as Hydrogen Donors

Reactants	Conditions	Percent Reaction
1,2-Diphenyl-1-p-tolylethane	400°, 5 min[a] tetralin	2%
"	400°, 30 min[b] tetralin	94%
"	400°, 5 min[a] vitrinite	50%
1,3-diphenylpropane	400°, 30 min[b] tetralin	23%
"	400°, 30 min[b] tetralin & vitrinite	43%
"	400°, 30 min[b] vitrinite	65%

a) The oven was at 400°, but the warm-up time is 15 minutes, thus the actual temperature was considerably less than 400°.
b) 30 min included warm-up time.

extent reaction — as determined by g.c. analysis of the products — after various contact times with tetralin or with vitrinite.

Another diarylalkane which is easily decomposed in the presence of excess tetralin or excess vitrinite is 1,3-diphenylpropane. The major products in both cases are toluene and ethylbenzene, although a multiplicity of minor products are produced. Also given in Table I are comparisons of the extent reaction of 1,3-diphenylpropane (400° for 30 minutes) a) with excess tetralin; b) with excess tetralin and vitrinite; and c) with excess vitrinite. The extent reaction in each case was estimated from the g.c. trace.

Since the reactions were monitored by g.c., which would detect neither nonvolatile polymeric material, nor high molecular weight products of reaction with vitrinite, it is possible that the vitrinite is acting not as a hydrogen donor, but merely as a catalyst, and that the source of the hydrogen for the hydrogenolyses comes from the 1,2-diphenyl-1-p-tolylethane or from the 1,3-diphenylpropane. To circumvent this problem, we heated benzophenone to 400° for one hour a) in the presence of excess tetralin, and b) in the presence of excess vitrinite. The major products are diphenylmethane and water, with traces of toluene and benzene. The reaction in tetralin proceeded to the extent of only 12%, whereas in the presence of vitrinite 35% reaction had occurred.

Reactions of Tetralin other than Hydrogen Donation

V. F. Raaen (3) showed recently that tetralin-1-^{14}C reacts with Wyodak coal at 400° (1 hour) to the extent that the pyridine-insoluble residue contains chemically bound carbon-14 equivalent to 5% tetralin by weight. Further, when the residue was reheated in normal tetralin (400°, one hour) the reisolated solvent contained no measurable amount of either tetralin-^{14}C or of naphthalene-^{14}C. There were, however, traces of labeled alkylated naphthalenes, which were identified by g.c. retention times as 1- and 2-substituted methyl- and ethylnaphthalenes. These products undoubtedly arise as a result of free radical intermediates. We therefore investigated the possibility that methyl- or ethylnaphthalenes could be produced by the reaction of tetralin with structures containing aromatic moieties separated by two or more methylene groups, or with aryl alkyl ethers. Both types of structure (4,5) are known to be present in different kinds and ranks of coal.

We heated several diarylalkanes and aryl alkyl or aralkyl ethers to 400° in tetralin for varying periods of time. Many of these reactions yielded measurable quantities of methyl- and ethylnaphthalenes in addition to other products. Typical are the reactions of 1,3-diphenylpropane and of phenetole, both of which were investigated with carbon-14—labeled species. The products were analyzed a) by gas chromatography combined with radioactivity monitoring of carbon-14—labeled products; b) by gas chromatography equipped with mass spectrographic analyzers (5); and c) by isolation of specific products using preparative g.c. (6) followed by nmr analysis (Varian XL-100 Spectrometer). Given in Tables II and III are the major products obtained — together with appropriate yields — from the reactions of 1,3-diphenylpropane and phenetole, respectively, with tetralin.

The 1- and 2-methylnaphthalenes were isolated and identified by nmr analysis. Their genesis from the reaction of 1,3-diphenylpropane-2-^{14}C (^{14}C=*) and tetralin was determined as follows:

PhCH$_2$$\overset{*}{\text{C}}H_2CH_2$Ph + (naphthalene structure) → (methylnaphthalene with *CH$_3$) + (ethylnaphthalene with *CH$_2$CH$_3$)

The mixture of ethylnaphthalenes was identified by g.c. retention times and radioactivity assay by means of the g.c. radioactivity monitor. Traces of methylindane

Table II

Major Products and Yields Obtained[a] on Heating 1,3-Diphenyl-
propane with Tetralin One Hour at 400°

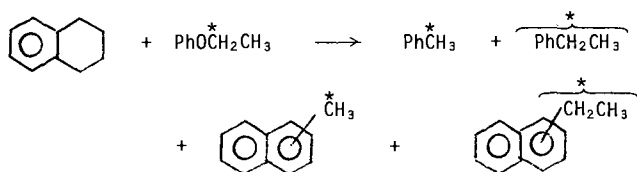|	
Toluene	28%
Ethylbenzene	19
1- and 2-(2-Phenylethyl) tetralins	8
1,4-Diphenylbutane	5
1- and 2-Methylnaphthalenes	3
Styrene	1.5
1,3-Diphenylpropene	1.5
Methyldihydronaphthalenes	
1,2-Diphenylethane	34
1- and 2-(2-Phenylethyl) naphthalenes	
Other	

[a]Based on 1,3-diphenylpropane consumed.

Table III

Major Products and Yields Obtained on Heating Phenetole
with Tetralin Eighteen Hours at 400°

Phenol	37%
Methylnaphthalenes	13
Toluene	7
Ethylbenzene	7
Ethylnaphthalenes	7
Methyltetralins	4
Ethylphenol	3
Ethyltetralins	3
Ethylmethylbenzene	
Methylindane	From Decomposition of Tetralin
Butylbenzene	

and of butylbenzene were always present after reactants were heated with tetralin.
That these latter two products were derived from tetralin was demonstrated by the
fact that they contained carbon-14 when tetralin-^{14}C was used in the reaction. In
like manner, labeled phenetole and tetralin were subjected to the conditions of
reaction with the following results:

It is clear from the isotopic labeling experiments that tetralin has entered into
the reaction both with 1,3-diphenylpropane and with phenetole. The results are
nicely accommodated by the postulation of radical intermediates. A possible
mechanism for the reaction of 1,3-diphenylpropane is indicated:

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THE CHEMISTRY OF COAL LIQUEFACTION

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This progress report presents a working hypothesis for our study of coal liquefaction with Illinois No. 6 coal and indicates the kinds of evidence on which our hypothesis is based and which are desirable for its substantiation.

Coal is considered to be mostly a crosslinked high polymer with condensed aromatic aggregates that are difficult to cleave and connecting links that are relatively easy to cleave (scissile bonds). A range of soluble materials is mixed with the predominantly insoluble material. Associated with these primary bond relations are significant interactions between phenolic groups and pyridine-type bases (1). Thus, relatively small polyfunctional molecules, even if not incorporated in the network, need complexing solvents to dissolve them. Our 1976 Coal Workshop paper related the molecular weight, and presumably the functionality, of the fractions that would dissolve in certain solvents (2), as revised and summarized in Table I. Recent experiments indicate that ethylene diamine will extract from coal much more and higher molecular weight materials at 120°C. An effort to relate the amount of soluble material extracted by solvents to the amount of solvent used and to the extent of swelling of the undissolved residue at 100° is in progress.
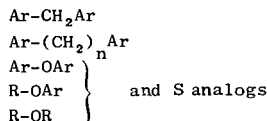
The extracted coal in the upper series of fractions in Table I is a preferred material for liquefaction studies, uncomplicated by admixed soluble materials. Progress in breaking bonds can be followed by formation of soluble materials and probably also by increased swelling of the insoluble material in a chosen solvent. The pyridine-soluble, toluene-insoluble fractions of both coal extract and SRC are preferred materials for following the upgrading of syncrudes. They have fairly high molecular weights and rather narrow molecular weight distributions. Both the extracted coal and the pyridine-soluble fraction have elementary analyses (dry, mineral free) and nuclear magnetic resonance (nmr) spectra (3) that are very similar; they apparently differ significantly only in molecular size.

Table I

Comparison of Fractions from Extraction and
Solvent-Refining of Illinois No. 6 Coal

	Insoluble extracted Coal	Soluble in Insoluble in	Pyridine Toluene	Toluene Hexane	Hexane	
	78.0	% C	79.5	83.0	84.0	More O
	4.8	% H	5.4	6.3	8.7	
	12.6	% O	10.8	7.3	5.0	
		Increasing C + H, decreasing O ⟶				
	All soluble	% C	86.1	87.4	89.9	More C + H
		% H	4.9	6.1	6.6	
		% O	5.7	4.0	2.0	
Common designations		Preasphaltenes, asphaltols, polar Compounds	Asphaltenes	Oils		
Average moleculer weight		~ 1200	~ 600	~ 300		

Coal
(78.6% C,
5.1% H,
12.4% O)

Pyridine extraction

Solvent refining

Fractions

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Figure 1 summarizes our data on retention times in gel permeation chromatography (gpc) as a function of average molecular weights by vapor phase osmometry (vpo) of fractions derived from both coal extract and the solvent-refined product from the same coal. Even though the SRC fractions contain about 10% more oxygen and 10% less carbon than the extract fractions, the points are well fitted by a single curve. Individual gpc curves show that fractionations into pyridine, toluene, and hexane-soluble fractions give products with fairly narrow and symmetrical gpc peaks. Two pairs of points in Figure 1 correspond to double peaks with special fractions.

Listed below are all the scissile bonds that we now think are important in the liquefaction of bituminous coal under common operating conditions. The same types of bonds are probably involved in scissions under strongly acidic conditions, as with phenol plus boron trifluoride etherate.

$$Ar-CH_2Ar$$
$$Ar-(CH_2)_nAr$$
$$\left.\begin{array}{l} Ar-OAr \\ R-OAr \\ R-OR \end{array}\right\} \quad \text{and S analogs}$$

We now consider current high-temperature, high-pressure liquefaction processes in terms of Table I and the scissile bonds listed above. The solvent-refining process consists mostly of conversion of insoluble coal to the pyridine-soluble, toluene-insoluble fraction of SRC. The net result approximates loss of some hydrogen and more oxygen, formation of a more aromatic aggregate, and some bond breakage. Because the solubility-molecular weight relations are the same in the extract and SRC series (2), the net phenol-base relations have changed little, and so the required bond breakage appears to be associated with net loss of ethers and some bibenzyl type bonds. The conversion of SRC to "oil" or distillate requires a large hydrogen input and a considerable reduction in molecular weight and heteroatom content. Part of the hydrogen requirement is to cap the fragments left when heteroatoms are removed as water, H_2S, and NH_3, but much of the hydrogen requirement may be to reduce condensed aromatic systems that cannot be cleaved to partially hydroaromatic systems that can be cleaved, especially by reforming catalysts.

Our working hypothesis leads us to suggest cheaper alternative routes to liquefaction. First, there are indications that ether clevage alone, without removal of oxygen or addition of hydrogen, can render coal soluble (4). The alkylation requirement now seems to be associated more with reducing phenol-base interactions (1,2) by O-alkylation (5) than with C-alkylation (4). There should be lower-temperature, low-pressure routes for ether cleavage, as by acids and bases, as well as the alkali metal route. Whether ether cleavage alone will take our coal to preasphaltenes, alphaltenes, or oils, or some of each (Table I) is under investigation (5).

Oxidations of coal models have shown that hydroaromatic rings are likely to be attacked first in free radical chain oxidations. We have therefore tried to dehydrogenate such rings to aromatic rings with two objectives, to direct the oxidation to the scissile bonds and to recover hydrogen for subsequent processing. Our first experiment with ethylene as hydrogen acceptor has given some promise of success.

We are also studying the possibility that selective oxidation will cleave most of the scissile bonds listed above. Oxidation of diarylmethanes should give ketones that can be converted to esters with a peracid. Longer aliphatic chains between aryl groups should be oxidized to pairs of acids. The alkyl ethers should be oxidized to esters. Hydrolysis of esters should then result in cleavage of scissile bonds. Mild oxidations of extracted coal with subsequent base hydrolysis have indeed given marked increases in soluble materials. Oxidation and nmr studies on soluble fractions of coal extract and SRC indicate that the extract is relatively rich in benzyl hydrogen atoms and that these are lost perferentially in oxidation; however, the SRC fractions that have the most aromatic hydrogen are most reactive and this kind of hydrogen is lost preferentially in oxidation.

We have also examined the use of commercial household bleach, ~ 0.8 M sodium hypochlorite, as an oxidizing agent at 30°, where extracted coal is very reactive. By stepwise oxidation, with removal of acids as they form, we have recovered 76% of the carbon reacting as carboxylic acids, mostly black and soluble only in aqueous sodium bicarbonate, with smaller proportions of water-soluble polybasic acids. The susceptibility of some, but not all, substrates to oxidation by sodium hypochlorite is pH dependent.

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(3) Kindly supplied by Prof. Alex Pines and Dr. D. E. Wemmer of the University of California, Berkeley.
(4) H. W. Sternberg and C. L. Delle Donne, Preprints, Division of Fuel Chemistry, 12 (4), 13 (1968); H. W. Sternberg, C. L. Delle Donne, P. Pantages, E. C. Moroni, and R. E. Markby, Fuel, 50, 432 (1971).
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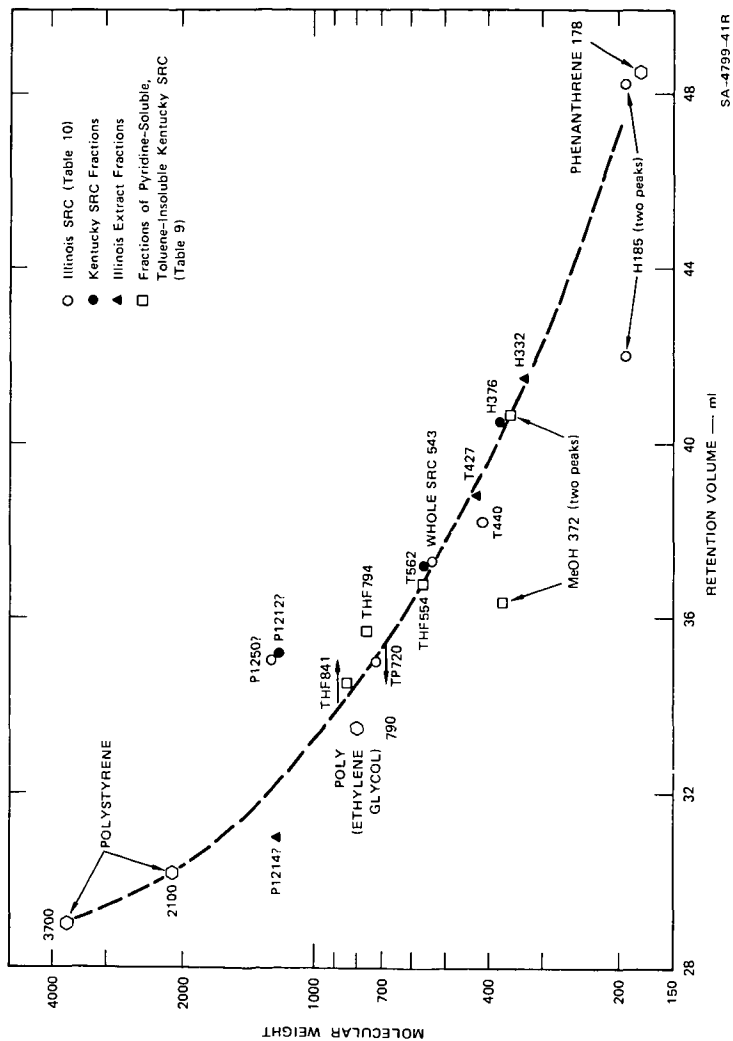
FIGURE 1   MOLECULAR WEIGHTS AND GPC RETENTION VOLUMES FOR FRACTIONS OF EXTRACTS AND SRCs
OF ILLINOIS AND KENTUCKY COALS

The letter associated with a point indicates whether the fraction was soluble in pyridine, toluene, or hexane.
The number is the $\overline{M}_n$ measured by VPO.

Early Stages of Coal-Carbonization:
Evidences for Isomerization Reactions*

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At temperatures between ∿350° and 425°C, the molecular structures that charac-
terize coal are rapidly, and very obviously, transformed into more stable carbon con-
figurations through loss of "volatile matter" (as tar and gas). But little is known
about possible configurational changes at lower temperatures. Thermograms of coal (1)
indicate specific heat effects as endo- and exotherms from ∿200°C up; but because en-
thalpy changes recorded in this manner include sensible heats as well as heats of
reaction, it is difficult to assess the nature of the chemical processes which produce
the thermograms. On the other hand, low-temperature chemical changes, if such did in
fact occur, should be reflected in the "reactivity" of heat-treated coal - and, in
particular in its response to oxidation; and if oxidation could be performed so as to
yield identifiable products, it should be possible to detect the major configurational
changes in the distribution of oxidation products.

Accordingly, since it was previously shown (2) that sodium hypochlorite oxida-
tion yields relatively simple carboxylic acids of which many could be identified by
gas chromatography (GC) and mass spectrometry (MS), we thought it pertinent to deter-
mine whether this technique, although involving still not fully understood reaction
paths, could also be used to monitor low-temperature changes in coal. The present
paper reports the first results of such an exploratory study.

Experimental and Results

For the purposes of this investigation, two coals - a Western Alberta lvb coal
with C = 90%, and a Kentucky hvb coal with C = 85% - were used.

10 g samples of these coals, each sized to -60 +115 mesh, were preheated in
helium for 2 hr at the desired temperature, cooled, and then stored under pure He
until required. No significant weight losses or changes in elemental compositions
were observed with either coal up to 375°C, but 5-10% weight losses, and slight (0.5-
1.2%) increases in carbon contents, with corresponding reductions in oxygen were noted
after preheating at 390-400°C.

For the oxidation experiments, 2 g (preheated) samples were first "activated"
by reaction with nitronium-tetrafluoroborate in acetonitrile, and thereafter treated
with 125 ml of an aq. 1.6 N sodium hypochlorite solution at 60°C. The pH of the re-
action mixture was maintained at 12 by adding NaOH pellets at regular intervals. When
reaction was complete, the mixture was acidified; insoluble matter was filtered off;
and soluble carboxylic acids were extracted with ether. The residual solution was
freed of water by low-pressure distillation at 40°C, and solid material left behind
was extracted with anhydrous methanol.

The ether- and methanol-extracts were then combined, converted to methyl esters
by reaction with diazomethane, and separated by gel permeation chromatography on a
(Water Associates') Poragel column into two fractions with molecular weights >600
and <600 respectively (fractions A and B). Fraction B (mol. wt. <600) was further
subdivided into "simple" (B,1) and "complex" (B,2) acids by elution chromatography
on a Florisil column. (From this column, methyl esters of "complex" acids could only

be eluted with 10:1 chloroform-methanol, while esters of "simple" acids could be taken off with pentane, hexane and 2:1 hexane-chloroform.)

The "simple" acids (fraction B,1) were quantitatively analyzed by GC on OV-17/ Chromosorb WHP and reference to peak area vs. concentration diagrams for authentic compounds. Where no authentic compounds were available for methyl esters of toluene carboxylic acids, concentrations were computed from response factors derived from those appropriate for the methyl esters of benzene carboxylic acids.

Detailed study of the oxidation products showed that the raw and variously preheated coals furnished substantially identical amounts of carbon dioxide (Figure 1), but that there were significant, though complex, variations in the yields of carboxylic acids (Figures 2-6) and that these yields depended on the nature of the coal as well as on the preheat temperature. Thus, while the lvb coal had to be preheated to at least 350°C before it produced greater than the initial amounts of carboxylic acids, the hvb coal needed only to be preheated to 200°C before doing so (Figure 2).

These observations accord well with enthalpy changes recorded by differential thermal analysis (1), and are, in our view, clearly indicative of thermally induced alterations of the initial carbon configurations in the two coals.

Fraction A - composed of acids with mol. wts. in excess of 600 - presumably represents condensed aromatic fragments of the original and heat-treated samples; and if so, the fact that yields of this fraction increase with preheat temperatures suggests that aromatization begins at temperatures as low as 150°C in hvb coal and at ~200°C in lvb coal (Figure 3).

Fraction B,2 - which represents over 50% of the total acid product from each sample and consists of "complex" acids with mol. wts. <600 - can be tentatively identified as originating in coal fragments that produce "pre-asphaltenes" in coal liquefaction processes (3), and variations of the yield of this fraction with preheat temperature are also interesting (Figure 4). In the case of lvb coal, B,2 yields reach a maximum at 375° and then decline precipitously at 390°C, but the decline is compensated by an almost eqivalent increase in the yield of high molecular weight (>600) material. In contrast, B,2 yields from the hvb coal attain a maximum at 200°C, fall to minimum at 300°C, and then rise to another maximum at 400°C.

The "simple" acids with mol. wts. <600 (fraction B,1), which were completely characterized and invariably accounted for 22-30% of the total acid products, are evidently produced from easily oxidizable open structured coal fragments; and from the lvb coal, the yield of this fraction decreased steadily as preheat temperatures rose. However, in the case of the hvb coal, the yield was found to remain constant up to 300°C, and to fluctuate thereafter (Figure 5).

Finally, some note must be taken of the distribution pattern of penta- and hexa-carboxy benzenes vis-a-vis that of tri- and tetra-carboxy toluenes. Quite generally, maxima for benzenes and almost coincident with minima and maxima of toluenes. But here again, significant differences between lvb and hvb coal are observed. For the lvb coal, maxima of benzenes lie at 175° and 375°C, while for the hvb coal, they appear at 350° and 400°C. Maximum yields of toluenes were obtained from lvb coal after preheating at 300°C, and from hvb coal after preheating at 150°C (Figures 6 and 7).

We believe that these variations in yield and distribution of carboxy acids are best understood in terms of low-temperature intra-molecular isomerization reactions which modify the initial carbon-hydrogen configurations of the coal well before it begins to undergo thermal cracking. Of the two specific processes that could be postulated as effecting such isomerization, one is trans-annular bond

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formation (Figure 8) and the other is isomerization of benzylic carbon to methyl-phenyl derivatives (Figure 8) and more complex ring systems. Either change could readily occur at temperatures as low as 150°C and create structures susceptible to oxidation by sodium hypochlorite.

We note, in this connection, that ether-oxygen also appears to play a major role in the behaviour of coal at elevated temperatures (4); but whether or not iso-merization and/or cleavage of ether-linkages also occur at low temperatures could not be determined in this study, since hypochlorite oxidation easily degrades hetero-cyclic functional elements under acidic as well as basic conditions.

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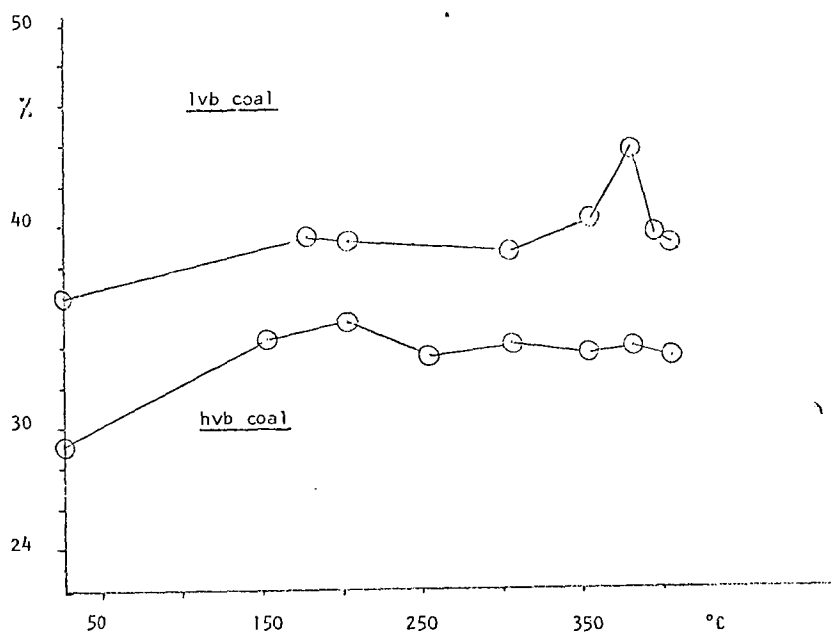
    B. Ignasiak and M. Gawlak; Fuel (Lond.) 56, 216 (1977)

Fig. 1 Yield of CO_2 as per cent of coal-carbon from variously
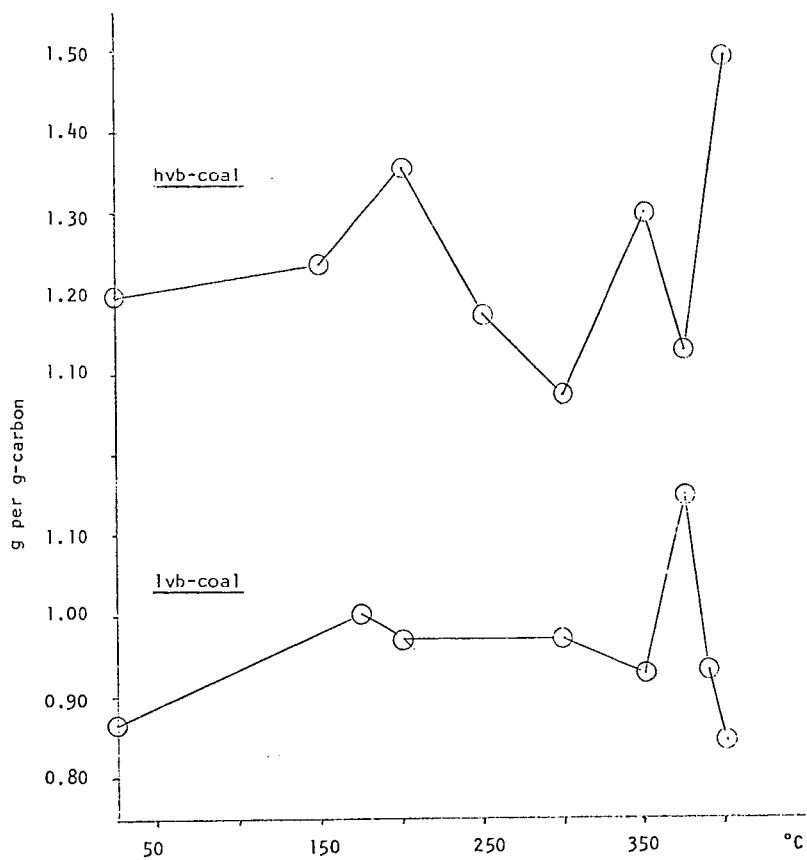heat-treated samples

Fig. 2   Yield of total carboxylic acids as methyl
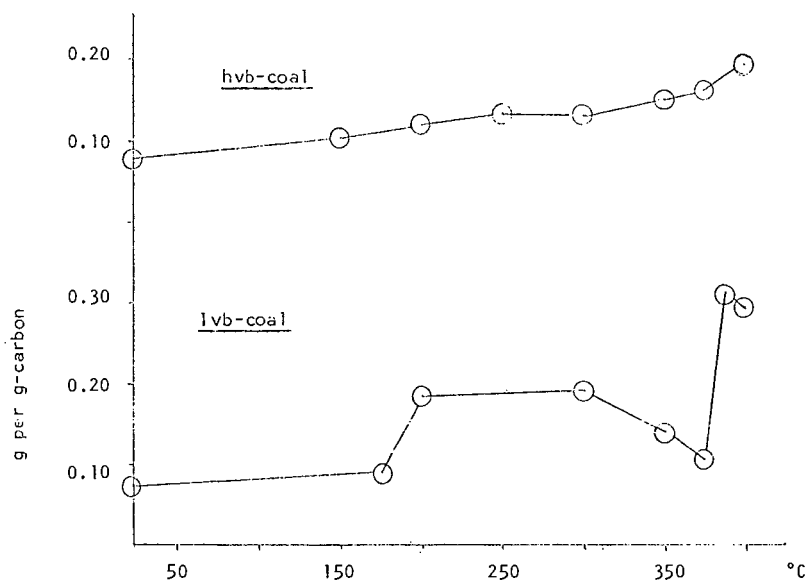   esters from variously heat-treated samples.

Fig. 3 Yield of 'complex acids' as methyl esters
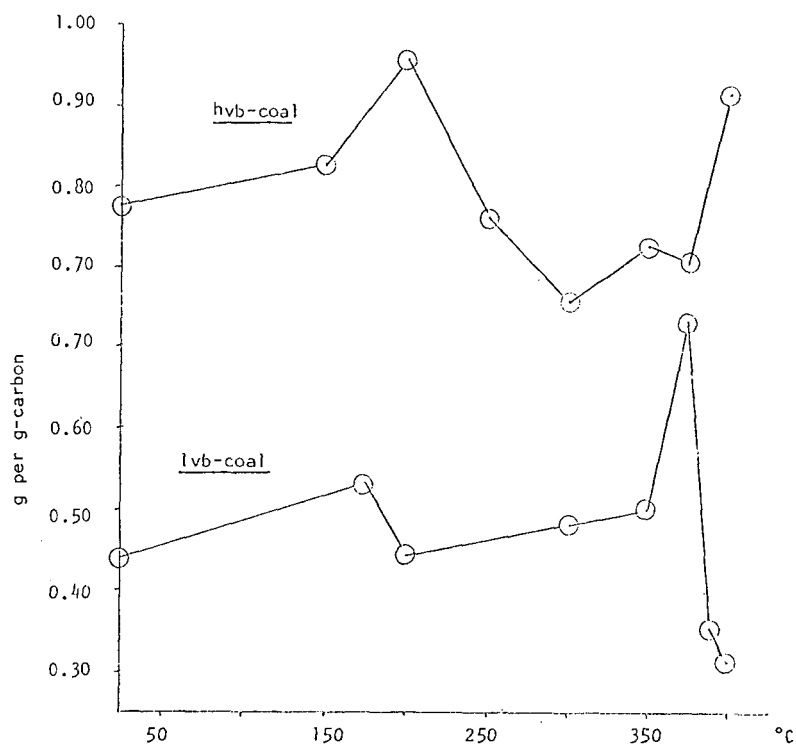Mo. Wt. >600

Fig. 4. Yield of 'complex acids' as methyl esters
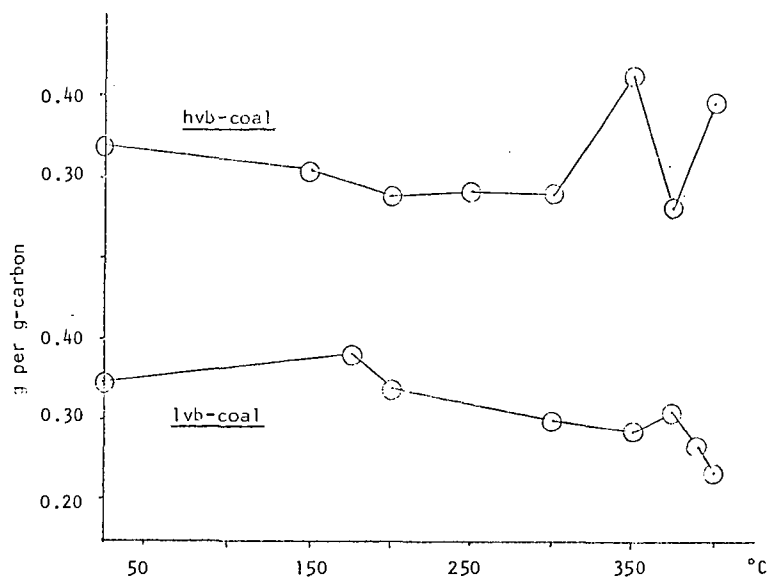Mol. Wt. <600

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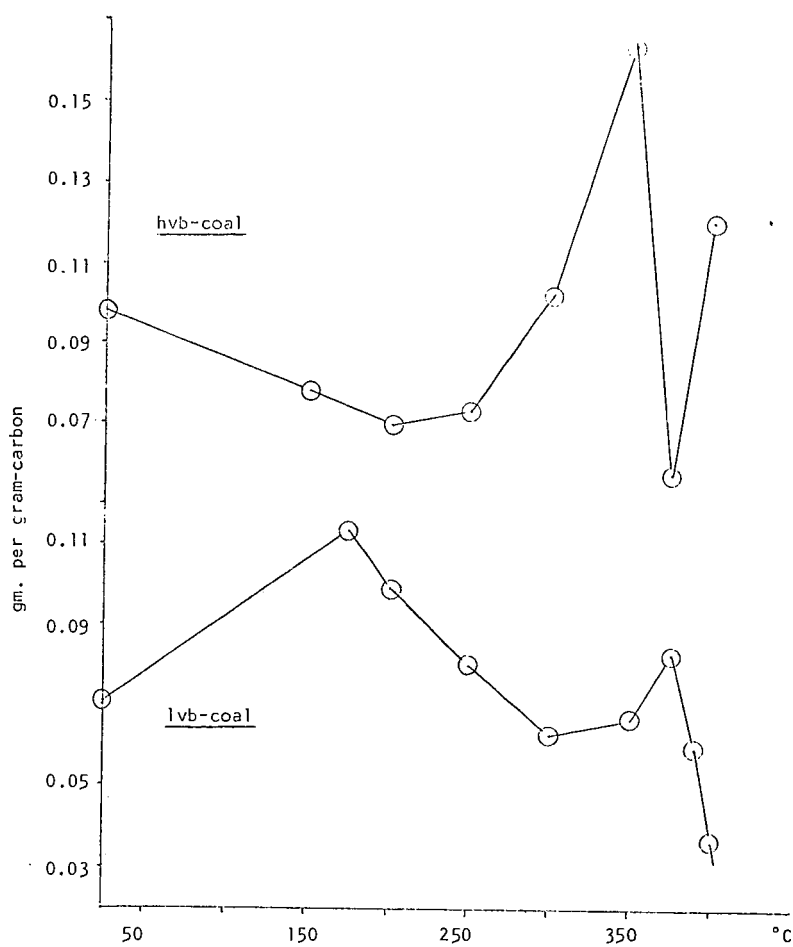Fig. 5 Yield of 'simple acids' as methyl esters.

Fig. 6 Combined yield of penta- and hexa-carboxyl benzenes.
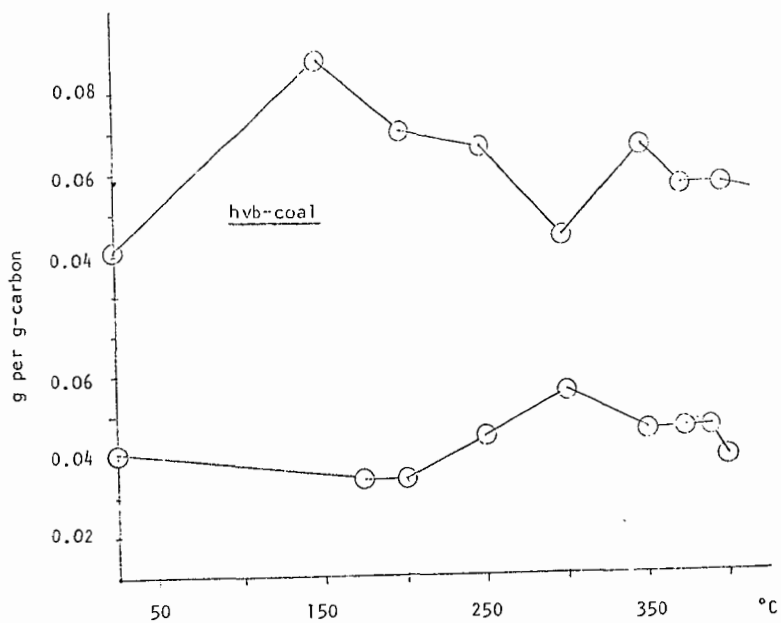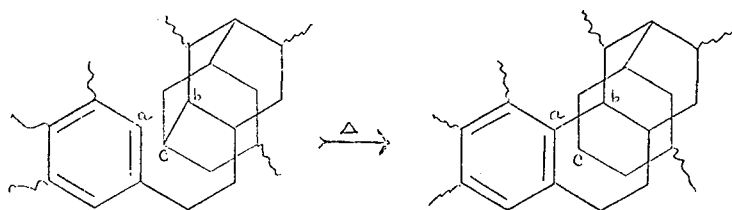
Fig. 7 Combined yield of tri- and tetra-carboxyl toluenes

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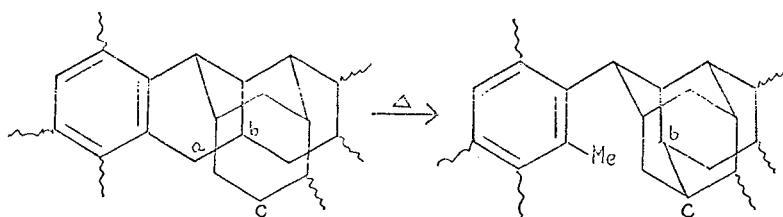
Scheme 1

Scheme 2

Fig. 8 Possible isomerization path.

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SUPERCRITICAL SOLVENTS AND THE DISSOLUTION
OF COAL AND LIGNITE

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The use of supercritical media as solvents in coal extraction is of interest because of their unusual solvent abilities. In a review of the general concept of supercritical gas extraction, Paul and Wise (1) discuss the solvent properties of materials above their critical temperatures (T_c). These supercritical vapors display unusual solvent powers when compressed to liquid densities. The solubility of naphthalene in supercritical ethylene (at 320 K), for example, is increased by a factor of 10^3 when the vapor density is increased from about 0.1 to about 0.6 g/cm^3 (2).

Whitehead and Williams applied this principle to the extraction of coal with hydrocarbons in their supercritical state (3). They extracted about 20% of a coal containing 38% volatile matter into toluene at 350°C (T_c for toluene is 318°C), or a quantity of extract that was greater than the tar yield from carbonization of the same coal.

In the work discussed here, we used a number of different solvents as coal dissolution media, all at temperatures above their respective critical temperatures. Our objectives were to investigate a possible structure/solvent-power relationship and to determine if the solvent has to be strictly above its critical temperature to be effective. Our experiments are briefly described below.
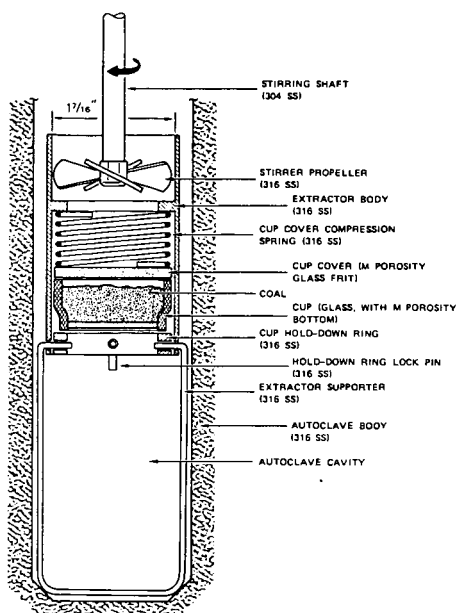
Experimental

All experiments were carried out in a 300 cm^3, 316 stainless steel, MagneDrive stirred autoclave from Autoclave Engineers. We used samples of beneficiated Illinois No. 6 coal, and a North Dakota lignite.* Most of the experiments were done at 335°C for 90 minutes.

It was necessary under these test conditions to be able to separate any materials soluble in the media from the material insoluble during the epxeriment. This precaution would eliminate any confusion of results in cases where a significant fraction of the coal was soluble at test conditions but insoluble when the system was brought back to ambient temperature and pressure. Accordingly, we designed a coal filter "basket" for these experiments (Figure 1). Our procedure was to place the starting coal between two sintered glass discs within the autoclave so that any material dissolved under our supercritical conditions would be carried through these discs and found outside the basket after the experiment.
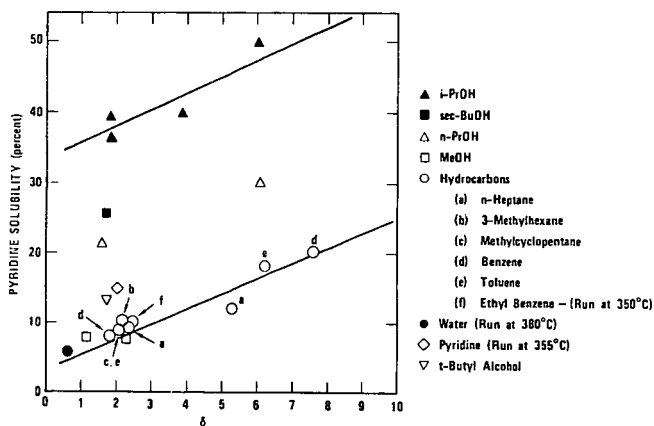
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* The samples were provided by Pennsylvania State University, whose designation for the coal samples was PSOC-26 and for the lignite, PSOC-246.

FIGURE 1 SUPERCRITICAL EXTRACTOR (TO SCALE)

FIGURE 2 HILDEBRAND SOLUBILITY PARAMETER, δ, VERSUS PYRIDINE SOLUBILITY OF COAL PRODUCTS
Experimental conditions were 335°C, 90 min.

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Results and Discussion

Supercritical Extraction

We performed a number of experiments with several media, both with and without the extraction apparatus (basket) in the reactor, and under identical experimental conditions. The results in Table 1 show that, first, the degrees of extraction are small, no more than about 13% for the best cases, and second, that the values for material dissolved in each medium after reaction are virtually the same both with and without the basket. Thus, the supercritical media are extracting up to about 13% of the substrate, and that extract in turn is soluble in the respective media at ambient conditions. The extraction for Run 86 is significantly low, perhaps because the lignite tended to agglomerate under the conditions of this experiment, thereby reducing circulation of i-propanol through the basket.

Clearly, filtration under supercritical conditions was not necessary to obtain the maximum dissolution, and the promise of supercritical extraction appeared diminished in view of the low extraction values. To confirm these findings, we made several additional runs with coal in a wide range of solvents without the basket at several different solvent densities.

We found it useful to consider all our extraction data in terms of the Hildebrand solubility parameter of the respective solvents. This parameter is a measure of the cohesive forces in a solution and is expressed by the relation $\delta = a^{1/2}/V$, where a is van der Waal's intermolecular term and V is the molar volume (4). In addition, the solubility parameter has been considered in terms of polar and nonpolar contribuions [4(c)]. The application of the solubility parameter to coal processing has been discussed by Angelovich et al. (5), who concluded that solvents with a nonpolar solubility parameter of about 9.5 appeared to be most effective in coal dissolution.

Giddings et al. (6) found a correlation between solvent capabilities and δ values of a number of supercritical fluids at liquid densities. Their expression defining the parameter is

$$\delta = 1.25 \, P_c^{\frac{1}{2}} \rho_r / \rho(\text{liq}) \qquad \qquad 1)$$

where P_c is the critical pressure in atmospheres, ρ_r is the reduced density, and $\rho(\text{liq})$ is the reduced density of liquids, assumed to be about 2.66. We can thus vary the δ value for a given medium simply by varying the experimental density.

The pyridine solubition of our starting coal is 13%. Figure 2 compiles all our extraction data and plots the total pyridine solubilities of the coal products versus the Hildebrand solubility parameter value for each medium, as determined by Equation 1. Each experiment yielded both a filtrate soluble in the reaction medium and a filterable residue. All filtrates were pyridine-soluble, and the solubilities in pyridine of each of the residues were determined at room temperature. The values used in the figure are the total solubilities, obtained by summing the fraction of the starting coal represented by the filtrate, and the pyridine-soluble fraction of the starting coal in the residue.

Table 1
SUPERCRITICAL EXTRACTION OF ILLINOIS NO. 6 COAL AND NORTH DAKOTA LIGNITE (at 335°C for 60 min)[a]

	Run No.	Supercritical Medium Type	(g/ml)	Mode	Recovered in medium[b] (%)	Mass Recovered (%)
Coal	55	iPrOH	0.3	Basket	11	97
	38	iPrOH	0.3	No Basket	11	97
	82	Benzene[c]	0.6	Basket	12	95
	60	Benzene[c]	0.6	No Basket	13	92
	58	MeOH[d]	0.4	Basket	12	97
	76	MeOH[d]	0.4	No Basket	8	94
Lignite	84	Toluene	0.2	Basket	3	87
	66	Toluene	0.2	No Basket	4	88
	86	iPrOH	0.1	Basket	5	86
	65	iPrOH	0.1	No Basket	12	85

[a] 5 g coal or lignite; reactor volume, 280 ml.

[b] Room temperature solubilities of the starting coal and lignited are less than 1% in all the test solvents.

[c] 1 g coal, for 3 hr.

[d] 1 g coal.

Table 2
EXPERIMENTS ON ILLINOIS NO. 6 COAL WITH TOLUENE BELOW AND ABOVE ITS CRITICAL TEMPERATURES FOR 90 MINUTES

Run No.	Solvent	Experimental Conditions P (g/ml)	Temp[a] (°C)	psig[b]	Filt[c]	Solubility (%) THF	Pyridine
45	Toluene (subcritical)	0.65	305	2400	8	12	13
49	Benzene (supercritical)	0.70	305	2400	8	11	13
27	Toluene (supercritical)	0.65	335	3400	13	21	24
16	Benzene (supercritical)	0.70	335	4100	10	22	20

[a] The critical temperatures for toluene and benzene are 320°C and 288°C, respectively.

[b] The critical pressures of toluene and benzene are 630 psi and 720 psi, respectively.

[c] The "Filt" values are the fraction of the product coal which is soluble in the test medium at room temperatures.

The plot may be roughly split into two regions. The upper region of relatively high pyridine solubilities represents data from previously discussed work with alcohols as H-donor solvents (7). The bulk of the data falls about the lower line. Most of the solubilities are below 13% or less than the solubility of the untreated coal itself in pyridine.

We used pressure ranging from about 700 psi for the lower δ values to about 4000 psi for the highest. Within the range of solvents studied, and with the exception of the H-donor alcohols, no gross differences are apparent between solvent types. For example, all the hydrocarbons (◯), both aliphatics and aromatics, cluster well about the line, as does the single point for water (●). Methanol (▢) is also close to the line and apparently does not serve as an H-donor* under these conditions. The two solvents a little above the line are pyridine (◇) and t-butyl alcohol (▽). Pyridine is a well known solvent in coal work; its extraction capability is apparently not enhanced by high pressures and temperatures and its supercritical state. The alcohol, on the other hand, cannot operate as an H-donor, and yet, unexpectedly, the plot shows it to be a better solvent than methanol.

The roughly linear correlation displayed by the data suggests that the dissolution process is not a function of the solvent type, but rather, is sensitive to the density (i.e., pressure) of the medium. Perhaps what we observe is an initial, reversible thermal fragmentation of a critical link in coal.

$$\sim\!\!\sim\!\!C\text{--}C\!\sim\!\!\sim \longrightarrow 2C\cdot$$

followed by some means of stabilization by solvent (S)

$$\sim\!\!\sim\!\!C\cdot + S \longrightarrow \text{stable product}$$

The nature of the stabilization process remains in question.

The positive slope of the lower line in Figure 2 suggests that greater degrees of extraction might be possible at higher δ values. The point labeled d in the figure is for a δ value of 7.5 and is taken from an experiment with benzene at 4100 psi. If we make the appropriate simplifying assumptions regarding liquid compressibility, we can calculate that for a δ value of 10, where by extrapolation we would expect a pyridine solubility of 25%, a pressure in excess of 7800 psi would be required. Clearly, extractions at thse pressure would not be practical.

Effect of Supercritical State

Finally, to determine if the supercritical state is stictly necessary to obtain the small extractions discussed here, we compare the results of using toluene and benzene at 305°C and 335°C. These temperatures are above the T_c of

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We have recently found that with some bases present, methanol operates very well as an H-donor alcohol.

benzene ($288\,^{\circ}$C), but below and above, respectively, the T_c of toluene ($320\,^{\circ}$C).
The results of this series of runs are presented in Table 2.

The benzene in Runs 49 and 16 is supercritical. With increasing tempera-
ture, a small increase can be seen in the tetrahydrofuran (THF) and pyridine
values. Similar changes can be seen for toluene in Runs 45 and 27 over the same
temperature range, where toluene is below and above its T_c, respectively.

The changes observed are due to temperature differences alone. These conver-
sions are thus due to the presence of a dense medium at high temperatures. We
conclude, therefore, that whether an extraction medium is strictly supercritical,
that is, above the critical temperature, is of little consequence.

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HETEROATOM SPECIES IN COAL LIQUEFACTION PRODUCTS

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INTRODUCTION

An assessment of the nitrogen and oxygen heteroatom species in coal-derived prod-
ucts is a complex yet important analytical problem in fuel chemistry. Principally,
this is because the system is a multifarious molecular mixture that does not easily
lend itself to direct analysis of any one component or functional group. Albeit
this problem is not new, the characterization of these heteroatoms is of immediate
importance to further processing of these fuels. We shall detail the methods and
techniques used to rapidly isolate and/or characterize both nitrogen and oxygen
heteromolecular species. Utilization is made of solvent separations, functional
group type separation, chemical derivatization, HCl salt formation and the use of
chromatographic and spectrometric analytical methods to quantitate our results.
Specifically, we ascertained the kind and distribution of nitrogen and oxygen
heteromolecules in a coal liquefaction product and in a recycle solvent used in
solvent refined coal (SRC) processing. The coal liquefaction product was first
solvent separated into oils, asphaltenes, preasphaltenes and ash, while low boiling
oils (light oils) trapped from knock-out tanks and the SRC recycle solvent were
treated directly. Nitrogen bases were complexed as HCl adducts or separated on
ion-exchange resins. Hydroxyl-containing species from the separated fractions were
quantitated by infrared spectroscopy or by formation of a trimethylsilyl ether
(TMS) and subsequent analysis by ^{1}H NMR and mass spectrometry. Hydroxyl species
were also isolated on ion-exchange resins or by selective gradient elution from
silica gel.

EXPERIMENTAL

Solvent Separation

Coal liquefaction products were solvent separated[1] by first freezing the coal
liquids in liquid nitrogen and grinding them to fine particles. This frozen oil
can be easily transferred to a stainless steel centrifuge tube. Pesticide grade
solvents were then used to solubilize specific fractions--oils (pentane), asphal-
tenes (benzene), preasphaltenes[2] (tetrahydrofuran) and coal-derived ash (insoluble
in all solvents used). By starting with a 3-4 gram sample, one (1) liter of each
solvent in four or five 200 ml portions was usually sufficient to extract the
solubles. Insolubles were removed by centrifugation at 10^4 rpm at 6°C for 10
minutes. Solvents were removed by nitrogen flush on a Rotovap using a water bath
(65-85°C). Asphaltenes were treated differently at the final solvent removal step;
a 20 ml solution of benzene/asphaltenes was swirled in a flask and flash frozen in
liquid nitrogen, and the solvent was sublimed at 10^{-1}-10^{-2} torr for 2-3 hours.

HCl Treatment

The objective of this procedure was to separate and/or concentrate both nitrogen
heteromolecules and hydroxyl-containing species from coal-derived material.[3] Gas-
eous HCl was bubbled through a benzene or pentane solution of the coal product to
form an insoluble HCl adduct with molecules containing a basic nitrogen atom. The
adduct, after being washed free of other components, was back titrated with dilute
NaOH solution to free the base nitrogen into an organic phase, usually diethyl
ether, methylene chloride or benzene. The two fractions recovered contain acid/
neutral and nitrogen base material, respectively.

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Hydroxyl Silylation

Oils, asphaltenes and preasphaltenes were treated with hexamethyldisilazane (HMDS) to form a trimethylsilyl ether (TMS) of active hydroxyl groups.[4,5] A 50 mg sample of coal-derived product was dissolved in 25 ml of benzene containing 50 μl of pyridine-d_5. To this solution 500 μl each of HMDS and N-trimethylsilyldimethyla-mine were added. This mixture was maintained as a closed system except for a small Bunsen valve and mildly refluxed for one hour with occasional swirling of the flask. After the reaction was completed, solvents and unreacted reagents were removed under nitrogen flush on a Rotovap and finally freeze dried from 5 ml of benzene for 30 minutes. A portion of the final product was checked by infrared spectroscopy (IR) for disappearance of the OH band at 3590 cm^{-1}.[6] The remaining sample was dissolved in benzene-d_6 and its proton NMR spectrum taken and inte-grated. From the relative areas of the peaks in the proton NMR spectrum, a percent H as OH was calculated (Equation 1).[7]

$$\frac{(\frac{\text{TMS Area}}{9})}{(\frac{\text{TMS Area}}{9}) + (\text{Remaining Proton Area})} \times 10^2 = \% \text{ H as OH} \quad (1)$$

From an elemental analysis of the original sample, one can calculate the weight percent oxygen as OH on a moisture and ash free basis (MAF).

Combined Gas Chromatography-Mass Spectrometry (GCMS):

The combined GCMS analyses were performed using a Dupont 490 mass spectrometer[*] in-terfaced to a Varian 1700 Series gas chromatograph, equipped with an 80:20 glass splitter and a flame ionization detector. The spectrometer was also coupled to a Hewlett-Packard 2100A computer used for spectrometric data storage and reduction. The mass spectrometer was operated at a resolution of 600 and an ionizing voltage of 70 eV. The ion source, jet separator and glass line from the chromatograph to the mass spectrometer were held at 275°C. The chromatographic effluent was con-tinuously scanned at a rate of four seconds per decade by the mass spectrometer.

The gas chromatographic separations were effected using a variety of conditions. The nitrogen bases and acid fractions from the coal liquefaction product were chromatographed on a 10' x 1/4" OD glass column packed with 100-120 mesh Supelco-port coated with 3% OV-17. Bases from the SRC product were chromatographed on a 10' by 1/8" OD glass column packed with 100-120 mesh Chromasorb-G coated with 2% OV-17. Gas chromatographic separation of bases from the light oil was achieved using a 10' x 1/8" OD glass column containing acid washed and silyl treated 100-120 mesh Supelcoport coated with 3% Carbowax 20M. In each case the He flow rate was 30 cc/min and the analyses were performed using appropriate temperature programming conditions.

Column Chromatographic Separation

Coal-derived liquids, soluble in pentane, were separated into five fractions: acids, bases, neutral nitrogen, saturate hydrocarbons and aromatic hydrocarbons. Acids were isolated using anion-exchange resins, bases with cation-exchange resins, and neutral nitrogen by complexation with ferric chloride adsorbed on Attapulgus clay. Those pentane soluble hydrocarbons remaining were separated on silica gel to give the non-adsorbed saturates and the moderately retained aromatics. This method is commonly referred to as the SARA technique.[8]

RESULTS AND DISCUSSION

The centrifuged coal liquid product (CLP) was produced using Ireland Mine, Pittsburgh seam, West Virginia coal in the 1/2 ton per day SYNTHOIL Process Development Unit (PDU).[9] Operating conditions for this experiment were 4000 psi hydrogen pressure, 450°C and no added catalyst. The light oils were derived from a catalytic experiment (Harshaw 0402T) using Homestead Mine, Kentucky coal, under 4000 psi pressure and 450°C.

The coal liquefaction product was solvent separated by the method previously described to yield the distribution of fractions given in Table 1. Figure 1 gives the atom weight percent distribution of nitrogen and oxygen in the solvent separated fractions listed in Table 1. The pentane soluble oils were subsequently separated into five fractions using the SARA chromatographic scheme. Table 2 lists the weight percents of the individual fractions. The asphaltenes were treated with HCl to form acid/neutral and base subfractions, 63 and 37 weight percent, respectively.

The acid and base fractions from the SARA separation of the oils were subjected to analysis by combined GCMS and low voltage low resolution mass spectrometry (LVLR). Figures 2 and 3 reproduce the gas chromatograms of the base and acid fractions, respectively. The oxygen containing species shown in Figure 3 have been classified as alkylated phenols, indanols/tetralinols, phenyl phenols, and cyclohexyl phenols. Table 3 lists the carbon number range and tentative compound type assignments for the nitrogen heteromolecules in the acid and base fractions as determined by LVLR mass spectrometry.[10] Table 4 lists the compound types assigned to the base fraction of the oils by GCMS.

Table 5 lists the carbon number range data from the HRMS analysis of the asphaltenes and their acid/neutral and base subfractions. It must be noted that at the operating conditions of the solids inlet, 300°C, 10^{-6} torr, less than 50% of the these materials could be volatilized. These preliminary studies have also indicated the presence of a limited number of diaza-species from Z# = 8-18.

The SYNTHOIL PDU contains several knock-out traps that condense low boiling components, light oils.[11] Nitrogen bases in the light oils were isolated by their precipitation with gaseous HCl and back titrated with NaOH into diethyl ether. These nitrogen bases constituted 3% by weight of the light oils. The gas chromatographic profile of these bases is given in Figure 4. An earlier study of these light oils characterized the saturates, aromatics and acidic components separated by Fluorescence Indicator Analysis (FIA).[12] The present investigation has resulted in the first quantitative analysis of pyridines and anilines in an oil produced by the hydrogenation of coal.

Table 6 summarizes the quantitative results from the chromatogram of Figure 4. It is of interest to point out that during this investigation, though numerous substituted pyridines were quantitated, no evidence for the parent was found. Because the techniques employed recovered components with boiling points near that of pyridine it is suggested that this observation may be significant. If free pyridine was trapped within the coal macromolecular structure it surely would have been found in either the light oils or the pentane soluble oils. If, on the other hand, pyridine was attached exo-, via a single C-C bond, to a more complex molecular network, the hydrogenation process should have freed it intact. But if the nitrogen heteroatom was an integral part of the original coal macromolecule, then hydrogenation would have cleaved a number of C_α-C_β bonds to produce a wide distribution of methylpyridines. Table 6 shows this methyl substitution trend. Quantitative results indicate that 2,3,6-trimethylpyridine is seven times more abundant than 2,3-dimethylpyridine and approximately twice as abundant as any other methylpyridine.

The source of anilines and, in particular, the observation of both the parent and the methyl substituted anilines are of interest. Anilines can arise from hydro-

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genation of the heteroring in a fused ring system followed by breaking of the bond between nitrogen and an aliphatic carbon.[13] Therefore quinoline and its alkyl derivative could be a source of the anilines. Table 4 lists seven quinolines found in the oils that could be the precursors.[15] The presence of the parent aniline, that should readily be hydrodenitrogenated,[13] is significant. If dealkylation was the same for all species, why didn't we see any of the parent pyridine? It could mean that the potential aniline moieties are located near the periphery of the coal macromolecule in contrast to the pyridines. The quantitative results indicate that methylanilines (toluidines) are in abundance in the order meta > ortho >> para > parent aniline, and all are greater than the dimethylanilines. These interpretations are based upon the more detailed analysis of the light oils. To date direct evidence for the presence of significant amounts of alkylated anilines and pyridines in the pentane soluble oils from the CLP have not been reported.

To complete this initial investigation of nitrogen species we chose to look at the nitrogen compounds present in the recycle solvent used for SRC processing and compare them with those found in coal liquefaction product oils. After extracting the gross benzene solubles, they were treated with HCl to isolate nitrogen bases. This particular sample had a slight residue that was benzene insoluble. Figure 5 gives the gas chromatographic profile of these nitrogen bases and summarizes the prominent structural isomers. The base fraction from the SRC solvent was less complex than the nitrogen bases found in the liquefaction oils, but the same principal molecular species were found in both samples.

The presence of hydroxyl groups in coal-derived materials has long been established. Our present interest is to define quantitatively the OH as a percentage of the total oxygen. The separation methods described concentrate a high percentage of the hydroxyl groups by anion exchange resin chromatography (acids) or the HCl treatment (acid/neutral). Once the separation/concentration has been made the sample is treated with a derivatizing reagent to form a trimethylsilyl ether, Ar-O-Si(CH$_3$)$_3$.

It has been shown that all of the hydroxyl groups contributing to the 3590 cm^{-1} infrared band can be quantitatively removed with the derivatizing reagent.[6] The TMS ethers are next examined by proton NMR. The signals near 0 ppm represent the trimethylsilyl (CH$_3$)$_3$ protons from each of the hydroxyl derivatives. By integrating the area under the total proton spectrum and allowing for the 9-fold intensity enhancement for the TMS area, the percent H as OH can be calculated. Table 7 lists some representative determinations of hydroxyl content from oils and asphaltenes. The silyl derivatization quantitation of hydroxyls in asphaltenes has been compared to the infrared spectroscopic method of standard additions.[14] Our results agreed[15] to within 10%. Infrared data, and those from others working on similar fractions indicates that there is little if any carbonyl oxygen (C=O) present in coal liquefaction products produced in the SYNTHOIL PDU. Therefore, we conclude that substantially all of the oxygen exists as either hydroxyl (phenolic or benzylic) or in an ether linkage (e.g. furan).

A useful corroboration of the NMR data and of characterizing the acid fraction of the oils is its mass spectrum before and after TMS derivatization. Figure 6 A and B shows the acid components from the pentane soluble oils before and after TMS derivatization, respectively. Note that the mass peaks are shifted 72 amu to give a nearly identical mass distribution. Table 8 lists those hydroxyl containing compounds that definitely formed a TMS ether. From the mass spectral data there was also evidence for trace amounts of indenol, naphthol and phenanthrol derivatives.

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Table 1. Solvent Separation Weight Percent Distribution.

Solvent Fraction	Wt. % of CLP
Oil	68.0
Asphaltenes	26
Preasphaltenes	4
Ash	2

Table 2. SARA Chromatography Fractions, Weight Percent Distribution.

Chromatography Fraction	Wt. % of CLP
Saturates	4.1
Aromatics	37.3
Acids	6.3
Bases	10.2
Neutral Nitrogen	3.9
Loss	7.4
Total Oil	68.0

Table 3. Carbon Number Distribution for the Acid and Base Fractions From SARA Chromatography Separation.

$Z\theta$	LRIV $C\theta$ Range	Bases Typical Structural Nitrogen Analogs	LRUV $C\theta$ Range	Acids Typical Structural Nitrogen Analogs
-5	6-12	Pyridines, Anilines	--	--
-7	8-13	Azaindans	--	--
-9	9-15	Dihydroquinolines, Indols	--	--
-11	9-15	Quinolines	--	--
-13	11-17	Phenylpyridines	--	--
-15	12-19	Azafluorenes	12-20	Carbazoles
-17	13-19	Acridines	14-20	Phenylindoles
-19	14-21	Benzo[ghi]azafluorenes	14-22	Benzo[def]carbazoles
-21	15-21	Azapyrenes	16-24	Benzocarbazoles
-23	17-26	Benzacridines	18-24	Phenylcarbazoles
-25	17-26	Benzo[ghi]azafluoranthenes	--	--
-27	19-26	Benzazapyrenes	20-29	Dibenzocarbazoles
-29	21-26	Dibenzacridines	22-29	Naphthylcarbazoles
-31	21-26	Azaanthanthrenes	22-29	Naphthobenzo[def]carbazoles
-33	23-26	Dibenzazapyrenes	24-29	Anthracenocarbazoles
-35	23-27	Azacoronenes	26-29	Anthranylcarbazoles
-37	--	--	28-29	Anthracenobenzo[def]carbazoles
-39	--	--	28-30	Dinaphthocarbazoles

Table 4. Compounds found in the nitrogen base fraction of Figure 2.

PEAK NUMBER	COMPOUND
1	SOLVENT (CARBON DISULFIDE)
2	PHENOL
3	CRESOL
4	CRESOL
5	TETRAHYDROQUINOLINE
6	QUINOLINE
7	6-METHYLTETRAHYDROQUINOLINE
8	METHYLQUINOLINE
9	ISOQUINOLINE
10	METHYLQUINOLINE
11	METHYLQUINOLINE
12	C_2-QUINOLINE
13	C_2-QUINOLINE
14	OCTAHYDRO-N-3-RING (OCTAHYDROACRIDINE)
15	METHYLOCTAHYDRO-N-3-RING (METHYLOCTAHYDROACRIDINE)
16	PHENANTHRIDINE + ACRIDINE
17	MEHTYLACRIDINE
18	AZAPYRENE
19	METHYLAZAPYRENE

Table 5. Carbon number range data for nitrogen heteromolecules in asphaltenes.

Z^a	Asph	Asph A	Asph B	Possible Structural Types
	Carbon Number Range			
-5	5-7	6,8,9	6	Pyridines
-7	8-11	9-12	8-12	Azaindans
-9	8-14	9-15	8-14	Dihydroquinolines; Indoles
-11	9-14	9-15	9-14	Quinolines
-13	11-16	11,12,14-17	11-16	Phenylpyridines
-15	11-19	11,12,14-19	11-17	Azafluorenes; Carbazoles
-17	13-20	14-20	13-18	Acridines
-19	14-20	14-21	14-19	Azabenzo[ghi]fluorenes
-21	15-21	15-22	15-20	Azapyrenes; Benzocarbazoles
-23	17-21	18-23	17-21	Benzacridines
-25	17-21	19-22	17-21	Azabenzo[ghi]fluoranthenes
-27	19-23	20-23	19-22	Azabenzopyrenes; Dibenzocarbazoles
-29	21-23	21-23	21	Dibenzacridines
-31	21-23	21,22	21,22	Azabenzoperylenes
-33	23,24			Azadibenzopyrenes

Formulas derived by HRMS represent isomers and fragment ions as well as molecular ions.

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Table 6. Identification and quantitation of selected peaks from nitrogen bases in light oils.

Peak #	Compound	Wt. % of Base Fraction
1	2,6-Dimethylpyridine	0.5
2	2,4-Dimethylpyridine	2.2
3	2,3,6-Trimethylpyridine	3.5
4	3,5-Dimethylpyridine	1.5
5	Aniline	6.4
6	2-Methylaniline	12.8
7	4-Methylaniline	8.1
8	3-Methylaniline	15.1
9	Quinoline	7.6

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Table 8. TMS derivatized hydroxyl species in acid components from SARA separation.

Molecular Weights		Molecular Weights	
Phenol Series	TMS Ether	Indanol Series	TMS Ether
94	166	134	206
108	180	148	220
122	194	162	234
136	208	176	248
150	222	190	262
164	236		276

Molecular Weights		Molecular Weights	
Acenaphthenol Series	TMS Ether	Fluorenol Series	TMS Ether
170	242	196	268
184	256	210	282
198	270	224	296
212	284	238	310
226	298	252	324
240	312	266	338
254	326	280	352

Table 7. Hydroxyl distribution in solvent separated fractions determined by TMS derivatization.

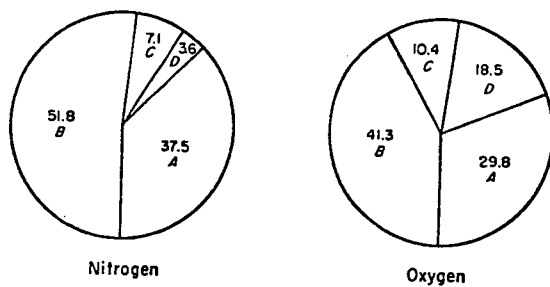| Fraction	% H as OH ±5%	% O as OH ±10%
Oils	1.2	67
Asphaltenes	2.0	43
Asphaltenes Acid/Neutral	2.0	44
Asphaltenes Base	1.5	49
Preasphaltenes	3.0	35

Figure 1. Atom weight percent distribution of heteroatoms.
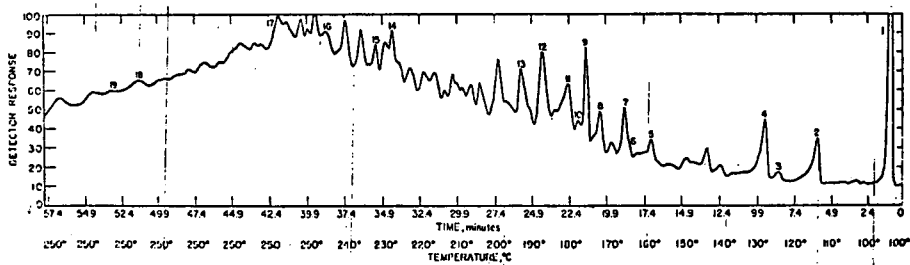A) Oils, B) Asphaltenes, C) Preasphaltenes, and
D) Ash.

Figure 2. Gas chromatogram of base fraction from a coal
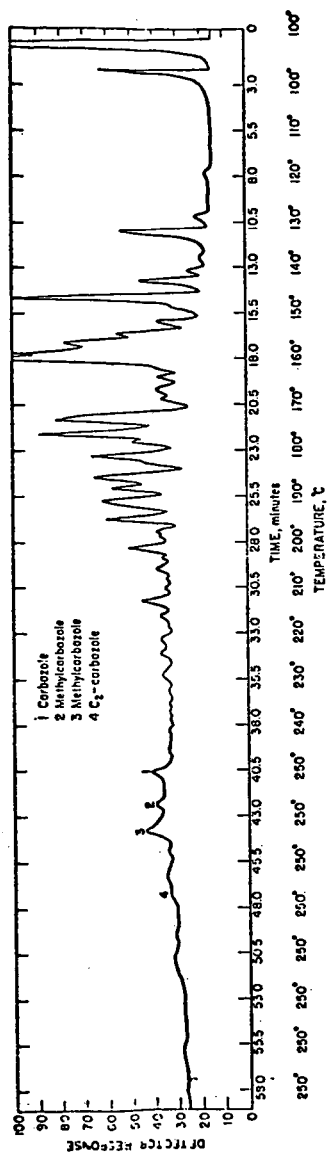liquefaction product. Table 4 identifies major
components.

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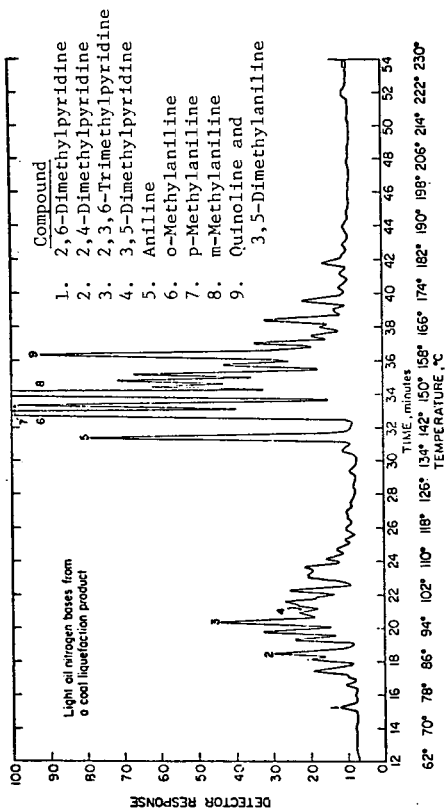Figure 3. Gas chromatogram of acid fraction from a coal liquefaction product.

1 Carbozole
2 Methylcarbozole
3 Methylcarbozole
4 C₂-carbozole

Light oil nitrogen bases from a coal liquefaction product

	Compound
1.	2,6-Dimethylpyridine
2.	2,4-Dimethylpyridine
3.	2,3,6-Trimethylpyridine
4.	3,5-Dimethylpyridine
5.	Aniline
6.	o-Methylaniline
7.	p-Methylaniline
8.	m-Methylaniline
9.	Quinoline and
	3,5-Dimethylaniline

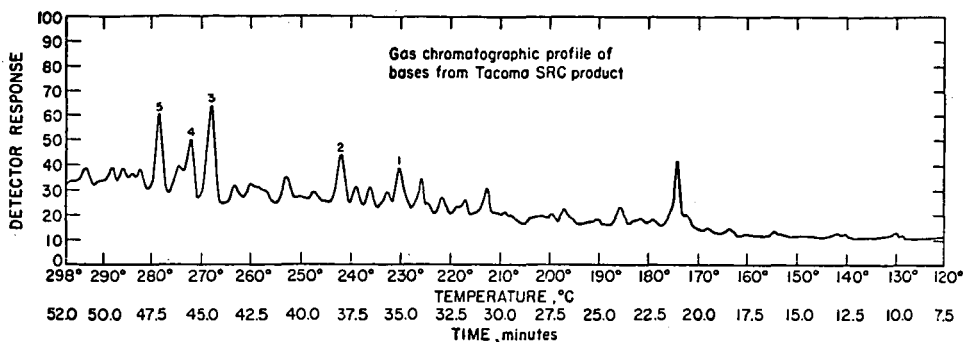Figure 4. Gas chromatogram of nitrogen bases from a light oil.

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Figure 5. Gas chromatogram of nitrogen bases from an SRC
recycle solvent. 1) N-3 ring, e.g. acridine,
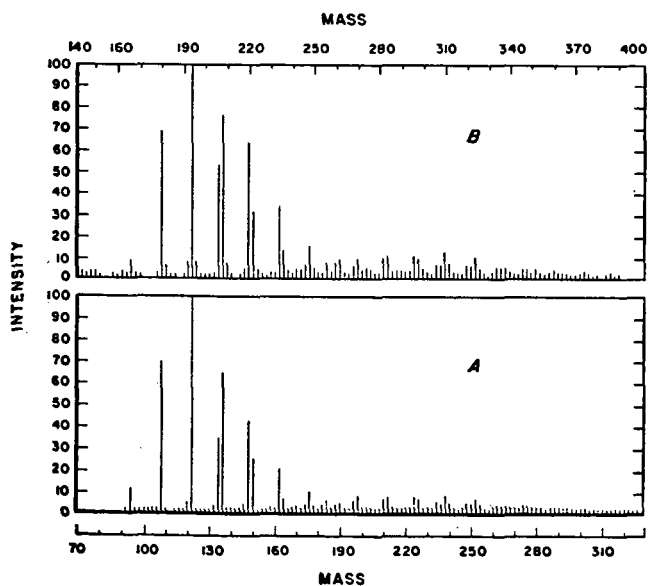2) methyl-N-3-ring, 3) azapyrene, 4)and 5)
methylazapyrene.

Figure 6. Mass spectrum of acids before (A) and after (B) TMS
derivatization. Note change in mass scale.

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Characterization of Coal Products
by Mass Spectrometry

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I. Introduction and Background

In studies on the organic chemistry of coal, the researcher, unfortunately,
is unable to examine a complete coal molecule. He must instead be content to
analyze bits and pieces of coal molecules produced by solvent refining, liquefac-
tion, pyrolysis, or extraction. Knowledge of the composition of these pieces helps
in understanding the organic chemistry of coal and is vital for the development of
coal liquefaction processes and the further upgrading of the liquefaction products.

Mass spectrometry is the prime technique used in our laboratories (1,2) and
in other laboratories (3) to determine the composition of the very complex mixtures
derived from coal. Petroleum fractions have been analyzed by mass spectrometry
(MS) for over 30 years. As heated inlet systems evolved (4,5) and instrumental
resolving power increased, MS was applied to higher boiling ranges and more complex
mixtures. When research in coal liquefaction began in our laboratories about 10
years ago, we had well-developed instrumentation, data handling procedures, and
quantitative analyses for petroleum (6,7). Extension of these techniques to coal
products required only minor changes and extensions (8,9). In this paper we
describe some of the MS procedures we use and give some typical examples of
analyses.

II. Equipment and Data Handling Procedures

A very repeatable low resolution instrument is used for streams in which the
major components have been previously identified. The unseparated naphtha boiling
range, separated saturate fractions, and mid-boiling range samples (when detailed
knowledge of the hetero-atom components is not required) fall in this category.
For mid-boiling and high-boiling fractions requiring more complete breakdown of
aromatic, hydroaromatic, and aromatic hetero-compounds, spectra are obtained on a
high-resolution double focusing instrument.

Both of the instruments are automated. A digital readout system senses
peaks and converts analog signals to digital signals, records digital data on
printed paper tape and on magnetic tape, and a larger computer reads the data
from the magnetic tape and further processes it employing proprietary computer
programs. A list of the equipment is shown below:

Item	Manufacturer	Model
Low Resolution MS	Consolidated Electrodynamics Corp.	21-103C
High Resolution MS	Associated Electrical Industries, Ltd.	MS50
MS Readout System	Columbia Scientific Industries	CSI-260
Printer	Mohawk Data Systems	2016
Computer	International Business Machines	370

III. Methods and Results

A. Naphtha Boiling Range

High ionizing voltage, low resolution spectra are adequate to determine
paraffins, naphthenes, 2-ring naphthenes, C_6-C_{11} benzenes, C_9-C_{10} indanes and

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tetralins, C_9-C_{10} indenes, C_{10}-C_{11} naphthalenes, and C_{10}-C_{12} phenols in the C_5 to 450°F boiling range. The calibration data were derived primarily from scans of pure compounds and assembled in a 20 component matrix. A summary analysis is given in Table I.

Table I

Component		Wt.%
Total Saturates		76.6
Total Benzenes		13.9
Indanes/Tetralins		2.3
Indenes		0.1
Naphthalenes		0.0
Total Phenols		7.1
	Total	100.0
Wt.Pct. Carbon		85.80
Wt.Pct. Hydrogen		13.09
Wt.Pct. Oxygen		1.11

With some assumptions regarding the molecular weight distributions of the paraffins and naphthenes, a useful elemental analysis can be readily calculated.

Occasionally more detailed data for the saturated components is desirable. A 42 component combined MS and gas chromatographic procedure determines the aromatic and phenolic components listed previously and further breaks down the paraffins into iso- and normal types by carbon number and the naphthenes into cyclohexanes and cyclopentanes by carbon number. Calibration data were obtained from pure compounds and from concentrates separated by molecular sieve and gas chromatography.

B. Higher Boiling Range Saturate Fraction

Fractions boiling above the naphtha range can be separated into saturate, aromatic, and polar fractions employing a modified version of the clay-gel adsorption chromatographic method, ASTM D-2007. The saturate fraction is analyzed by the high ionizing voltage MS method, ASTM D-2786. A typical analysis of a 430-950°F saturate fraction from a Synthoil product (10) is given in Table II.

Table II

Compound Type	Wt.%
Paraffins	34.2
1-Ring Naphthenes	18.4
2-Ring Naphthenes	16.3
3-Ring Naphthenes	14.6
4-Ring Naphthenes	10.3
5-Ring Naphthenes	3.0
6-Ring Naphthenes	1.1
Monoaromatics	2.1

Normal paraffins generally comprise the major part, 80-90%, of the total paraffins in coal liquefaction products and a lesser part in coal extracts. When a split between iso- and normal-paraffins is desired, gas chromatography rather than mass spectrometry is normally the method of preference in higher boiling

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fractions. Iso-paraffins are not usually identified. However, we have recently identified the isoprenoid paraffins pristane, 2, 6, 10, 14-tetramethyl pentadecane, and phytane, 2, 6, 10, 14-tetramethyl hexadecane in coal extracts and liquefaction products. These components were separated and identified by gas chromatography, corroborated by MS (10).

Isoprenoid paraffins are used in organic geochemistry to group oils into "families" (11). It is possible that coals from different seams or deposits might be differentiated by the relative ratios of these isoprenoids or by the isoprenoid to n-paraffin ratio. Pristane is thought to be derived from the diterpenic alcohol phytol (12), that comprises about 30% of the chlorophyll molecule, and its presence and concentration might be related to the environment of the marsh in which a particular coal bed or seam was formed.

C. Higher Boiling Range Aromatic and Polar Fractions

If data on the saturate portion are not required, the aromatic and polar aromatic components are determined on the unseparated sample. This is done with a high resolution instrument operated in the low ionizing voltage mode (13). The same procedure can be applied to separated aromatic and polar fractions, and this is preferred if there is a significant concentration of polar components.

With low ionizing voltage electrons only those components containing double bonds, such as aromatics and olefins, are ionized and only the molecular ion is produced. Thus, the spectra, the spectral interpretation, and the calibration data are simplified, as there is no interference between components.
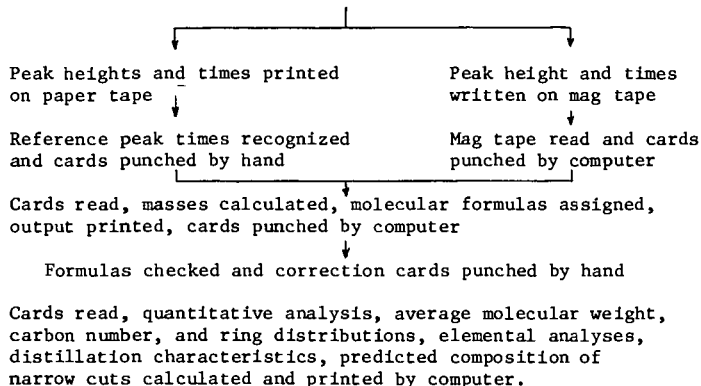
A full discussion of high resolution mass spectrometry is beyond the scope of this paper, so the technique will be described here only briefly. Different combinations to form molecules of the atomic species found in coal products will have different molecular weights. For example, from the atomic weights of the most abundant species given below one calculates the molecular weight of methyl

Atomic Species	Atomic Weight
Carbon	12.000
Hydrogen	1.0078
Oxygen	15.9949
Nitrogen	14.0031
Sulfur	31.9721

acenaphthene, $C_{13}H_{12}$, to be 168.0939, and the molecular weight of dibenzofuran, $C_{12}H_8O$, to be 168.0575. The high resolution MS resolves these two peaks having the same nominal molecular weight and the resolving power required is 4615 (Mass/ΔMass = 168/0.0346 = 4615). Other molecules require even greater resolving power to separate, particularly those containing nitrogen or sulfur (14). The MS and its auxiliary apparatus must also provide data from which precise mass measurements can be calculated. By measuring the time at which each peak occurs in a repeatable logarithmic scan of the spectra and by introducing compounds having peaks at known masses, the masses of the sample peaks can be determined very precisely, and the mass determines the molecular formula.

The scheme we use from mass spectrometer to final quantitative analysis is given in the data flow scheme shown below. The MS, MS readout system, printer, computer, computer programs, and people are required.

Sample and reference compounds charged to high resolution MS

Peak heights and times printed on paper tape

Peak height and times written on mag tape

Reference peak times recognized and cards punched by hand

Mag tape read and cards punched by computer

Cards read, masses calculated, molecular formulas assigned, output printed, cards punched by computer

Formulas checked and correction cards punched by hand

Cards read, quantitative analysis, average molecular weight, carbon number, and ring distributions, elemental analyses, distillation characteristics, predicted composition of narrow cuts calculated and printed by computer.

The most detailed information calculated from the high resolution spectra is the quantitative amount of each compound type at each carbon number. This tabulation is printed on 6 pages, 50 rows and 12 columns per page. This is more data than most engineers care to examine; therefore, summary tables, distributions, and other items are calculated from these detailed data. Excerpts from the compound type summary of a Synthoil product (10) are given in Table III. This is the initial summary made from the detailed data.

Table III

Compound Type	Wt.%	Average Mol.Wt.	Average Carbon No.	C Atoms in Sidechains
Alkyl Benzenes	1.74	160.8	11.9	5.9
Naphthalenes	11.02	176.4	13.5	3.5
Dibenzothiophenes	0.33	210.9	13.9	1.9
Fluorenothiophenes	0.16	241.2	16.4	2.4
Benzofurans	0.56	210.9	14.6	6.6
Dibenzofurans	2.55	255.0	16.1	4.1

The distribution of aromatic rings is a further summary which may be of value in refining of coal products. The ring distribution for the same product of Table III is shown in Table IV normalized to 100%, but the program also calculates and prints the same distribution normalized to the percent aromatics in the sample.

Table IV

	Hydrocarbons	Sulfur Comp.	Oxygen Comp.	Totals
Nonaromatics	0.0	0.144	0.0	0.144
1 Ring Aroms	20.960	0.517	2.235	23.712
2 Ring Aroms	36.919	0.611	3.465	40.996
3 Ring Aroms	15.644	0.153	2.202	17.999
4 Ring Aroms	12.388	0.067	1.470	13.925
5 Ring Aroms	1.997	0.020	0.208	2.225
6 Ring Aroms	0.856		0.084	0.940
7+ Ring Aroms	0.068			0.068
Totals	88.832	1.512	9.664	100.008

Additional calculated items, such as distillation characteristics (15), can be of great value to a researcher. If there is insufficient sample available for actual distillation, say from a bench-scale experiment, a few milligrams will suffice for a high resolution MS run. The calculated MS values, GC distillation, and 15/5 distillation are in good agreement.

The same high resolution scheme can also be applied to the polar fractions from the clay-gel separation. But the analysis of polars can become very tedious – the composition is much more complex as the polars contain many of the same hydrocarbon species as the aromatic fractions in addition to the polar hetero-aromatic oxygen, nitrogen, and sulfur compounds. In addition, our computer programs for some of these classes of components are not yet fully integrated into the final quantitative analysis program, and separate programs must be run and the results meshed. An indication of the complexity of the polar components in coal products is provided by a very small portion of spectra of the polar faction of a Synthoil product given in Table V, in which some typical multiplets resolved by the high resolution MS are shown. The data were obtained at a resolving power of about 40,000.

Table V

Mass	Formula	Intensity	General Formula	Possible Structure
254.0764	$C_{16}H_{14}SO$	230	$C_nH_{2n-18}SO$	C_2-Hydroxythiophenoacenaphthene
254.1306	$C_{17}H_{18}O_2$	822	$C_nH_{2n-16}O_2$	C_4-Dihydroxyfluorene
254.1671	$C_{18}H_{22}O$	511	$C_nH_{2n-14}O$	C_6-Hydroxyacenaphthene
381.1517	$C_{29}H_{19}N$	337	$C_nH_{2n-39}N$	C_2-Dibenzoperylenide
381.1729	$C_{26}H_{23}NO_2$	219	$C_nH_{2n-29}NO_2$	C_5-Dihydroxybenzochrysenide
381.2092	$C_{27}H_{27}NO$	363	$C_nH_{2n-27}NO$	C_7-Hydroxydibenzcarbazole
381.2456	$C_{28}H_{31}N$	267	$C_nH_{2n-25}N$	C_9-Chloranthridine
394.1357	$C_{30}H_{18}O$	110	$C_nH_{2n-42}O$	C_2-Hydroxybenzocoronene
394.1569	$C_{27}H_{22}O_3$	225	$C_nH_{2n-32}O_3$	C_5-Trihydroxybenzoperylene
394.1933	$C_{28}H_{26}O_2$	275	$C_nH_{2n-30}O_2$	C_6-Dihydroxybenzochrysene
394.2295	$C_{29}H_{30}O$	507	$C_nH_{2n-28}O$	C_9-Hydroxybenzopyrene

III. Conclusions

The national need to develop liquid fuels from coal to augment diminishing petroleum fuels is a challenge to the coal chemist. Analytical characterization of these coal liquids is a challenge to the analytical chemist. We believe that mass spectrometry, both low resolution and high resolution, plays an important role in responding to this challenge, and have given examples of the application of the technique to various coal product samples.

More detailed information on the use of high resolution mass spectrometry to analyze hetero-compounds in coal extracts and liquefaction products is given in our paper in the "Symposium on Refining of Coal and Shale Liquids," Division of Petroleum Chemistry, National ACS meeting, Chicago, 1977.

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FIELD IONIZATION AND FIELD DESORPTION MASS SPECTROMETRY
APPLIED TO COAL RESEARCH

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Mass spectrometry offers a unique way to characterize coal liquefaction products. Molecular weight profiles of such complex mixtures of organic materials may be considered as the first step in the understanding of their nature in molecular terms. Molecular weight profiles may be produced by nonfragmenting mass spectrometry, which almost exclusively yields molecular ions. Field ionization produces molecular ions from most organic compounds (1). When a complex mixture is analyzed by this mass spectrometric technique, we obtain a single peak for each constituent or for a group of constituents that shares the same nominal molecular weight. By repeated multi-scanning, we can obtain a quantitative molecular weight profile of complex mixtures (2).

The detailed molecular weight profiles attainable by field ionization mass spectrometry are much more informative than molecular weight profiles obtained by gel permeation chromatography (GPC). Moreover, GPC is subject to artifacts caused by associations of solutes or by solute-solvent complex formations. The average molecular weight profiles obtained by vapor phase osmosis (VPO) contain minimal chemical information and are useful mainly in conjunction with prior chromatographic separation. The cost per mass spectrometric analysis is higher than by these two techniques, but the information obtained on each individual constituent or group of constituents would cost much more if obtained separately by other techniques. The advantage of the mass spectrometric technique is its universality; for the same sample, the same molecular weight profile will be obtained by different investigators using different mass spectrometers.

Low energy electron impact ionization, which induces relatively little fragmentation, has been proposed as an appropriate alternative technique for the analysis of complex organic mixtures (3,4) including fuels(5). However, an excellent systematic study by Scheppele et al (6), has shown that field ionization is by far superior for this purpose. This recent study has shown that the relative ionization efficiencies by field ionization of many different classes of organic compounds are very similar, ranging only over a factor of two. This can be compared with a range of over an order of magnitude for low energy electron impact on the same substrates. Moreover, it was shown (6) that once corrected for the small differences in ionization efficiencies, which can be programmed and calculated for known homologous series, the analysis of complex mixtures, like fuels, can produce quantitative results with a significantly lower variance than obtainable with low energy electron impact, following an identical computational correction.

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Without such a correction, when dealing with <u>unknown</u> constituents, field ionization is <u>by far</u> a superior technique for obtaining semiquantitative information on the composition of highly complex mixture.

Field ionization is facilitated by the high field gradient that can be produced with very high curvatures. A cathode with a radius of curvature of about 0.1 μ requires less than 1000 V to produce field ionization. Such a configuration is readily attainable in a reproducible manner by the appropriate technology. At SRI, we have developed a novel field ionization source, the preactivated foil slit type source (7). This source is superior to the now classical SRI multipoint source (2,8) because of its lower sensitivity to deactivation in the presence of oxygen-, sulfur-, or halogen-containing compounds. The new source comprises an activated tantalum foil on which carbonaceous dendrites are deposited from pyridine vapor at high temperature under a high electrostatic field (7).

The mass analyzer used by us for multicomponent analysis is a 60° sector, 25 cm instrument and has been described before (9). The temperature of the sample can be controlled independently of the temperature of the source. The temperature of the source is maintained constant and higher than the maximum temperature the sample is subjected to; this prevents memory effects and results in more controlled ionization conditions. This ionization source, which may be operated up to 400^oC, may thus handle thermally stable compounds of very low volatility (9).

The ionization efficiency of our sources is 5×10^{-4} or higher, (10) which is comparable to that of advanced electron impact sources. However, owing to the relatively large area of our ionization source, the high energy of the ions produced, and their divergence, less than 10^{-4} of the ions produced are detected after mass separation. The overall efficiency of the present generation of field ionization mass spectrometers is about 2×10^{-8} ions/molecule for instruments with a magnetic sector analyzer and a resolution of 700.

Since most organic compounds have similar field ionization efficiencies (6), the molecular weight profile obtained by integrating all the spectra while evaporating the sample to completion truly represents the composition of the mixture. A number of examples of molecular weight profiles of different coal liquefaction products have been presented elsewhere (9). These spectra were obtained on our mass spectrometric system before it was interfaced with a PDP-11 computer. In this mode of operation, the mass range of interest was scanned repeatedly and synchronized with a 4096-multichannel analyzer operating in the multiscaler mode (8). The instrument integrates the spectra produced in each scan into a composite mass spectrum. The integration over time is necessary because the sample is evaporated slowly and the composition of the vapor phase changes because of the wide range of volatility of the different components. This field ionization mass spectrometric system thus facilitates the quantitative analysis of molecular weight profiles of mixtures that may contain constituents varying in their vapor pressure by many orders of magnitude (estimated range, 10^{10}) over a mass range up to 2000 amu with a resolution of $M/\Delta M$ = 800.

Computer Controlled FI Multicomponent Analysis

The published field ionization spectra of coal liquefaction products (9) are just the first step in the full utilization of field ionization mass spectrometric multicomponent analysis. These are chart recordings from a 4096-channel analyzer and, although the information in each channel is digitized, these spectra give us only a means of visual inspection of the gross feature of the spectra. Accurate mass assignment and the integrated ion counts under each peak are lacking, and these are necessary for any detailed quantitative interpretation of these complex spectra.

We would also like to know the "history" of each peak—the actual rate of accumulation of the ions of a given nominal molecular weight as a function of time and temperature of the analyzed sample. This information is necessary for estimating the number of materials of the same nominal molecular weight that contributed to a given peak. Moreover, from the temperature profile of a given peak, it may be possible to deduce whether some of the contributing ions originate from a chemical process (e.g., pyrolysis, dehydrogenation) that took place in the sample while the sample probe was being heated. Obtaining, for instance, a material with a molecular weight of only 150 when the probe temperature reaches $300^{\circ}C$ suggests that it may be a secondary pyrolytic decomposition product. The temperature profile analysis may help us to distinguish between these two possibilities and even determine the activation energy for the appearance of the given species.

To achieve these goals, we have interfaced our mass spectrometric system with a PDP 11/10 dedicated computer (Fig. 1). The computer controls the magnet scan of the mass spectrometer by means of the 12-bit digital-to-analog converter (DAC). The data acquisition program increments the input to the DAC at precisely controlled time intervals so that each channel is receiving ions counted for exactly the same amount of time. At the end of each time interval, the computer causes the ion counts accumulated by the 10-MHz counter to be transferred to the 12-bit buffer register. The counter is cleared and restarted in less than one microsecond, so the interface has a negligible dead-time and no ion counts are missed. The DAC input is incremented by one unit, and the ion count in the buffer is transferred to the computer and added to the previous ion counts for that channel. The time spent at each channel, or in other words, the scan rate of the mass spectrometer, is variable and is controlled by the operator through the data acquisition software. Actual time intervals are measured within the computer by a programmable clock based on a very stable quartz crystal oscillator.

The output from the DAC is a linear voltage ramp, since each of the 4096 possible channels is active for an equal amount of time. Since the mass of the ions focused on the mass spectrometer's detector varies as the square root of the magnet current, the magnet scan control unit is used to convert the linear voltage ramp into a signal that drives the magnet power supply to produce a linear mass scan.

The 12-bit analog-to-digital converter (ADC) is connected to a temperature programmer for the solids probe. At the end of each mass spectrometer scan, the temperature of the probe is recorded for later use in the printed reports or data analysis. Since the temperature programmer is digitally driven, a given temperature program can be very precisely reproduced to allow meaningful comparisons between samples. Our experience indicates that most pure compounds are volatilized over a narrow temperature range of $10-30^{\circ}C$. Thus, separate peaks will be observed in

the temperature profile of a single mass if there is more than one component of the sample with that particular molecular weight. It is possible to distinguish between genuine low molecular weight components of a sample and those resulting from the thermal decomposition of much larger molecules because these two different types of species appear at very different temperatures. Our experiments show no indication of significant pyrolysis of coal liquefaction products or of crude oils.

The report program produces reports listing the masses and total ion counts for each peak in the spectrum. Two different formats are available: one is a simple table of the peak mass and intensity, and the other is the same information arranged in a fixed format with 14 masses in each row. The advantage of this second format is that homologs are all listed in the same column, making it easy to pick out groups of peaks that may have similar chemical structures.

The plotting program produces simple bar graphs of the mass spectra on the X-Y recorder. Full-scale intensity is arbitrarily chosen as 50 and the entire spectrum is automatically scaled, if necessary, by dividing all peak intensities by an integer. Figure 2 is an example of a spectrum plot obtained in this manner. These spectra are evidently superior in quality to those obtained with the multi-channel analyzers (9).

Additional programs are available for performing simple but useful data handling tasks. These include programs for listing on the terminal the ion counts in each channel of a raw data file and a program for summing the data in several files into a composite spectrum. The latter program is useful for obtaining the molecular weight profile of a complex multicomponent mixture by adding together all the spectra obtained from a sample.

Additional examples of the types of information currently available from the combination of FIMS and the PDP 11/10 computer are shown in Figs. 3a and 3b. The sample was fractions 1 and 2 of basic compounds from an H-coal product and was provided to us by the Atlantic Richfield Company. The evolution of this spectrum as a function of temperature is presented in Figs. 3a and 3b. This figure presents the plotted spectra integrated within the different temperature ranges during the evaporation of a single sample.

The first three spectra in Figure 3a show volatile components of the sample that came off as soon as the sample was introduced into the mass spectrometer. When the signal produced by these volatile materials began to decrease, the operator started the temperature program, heating the sample at about $2^{\circ}C$ per minute. The heating rate was increased twice during the run to maintain a reasonably high signal as the less volatile components were being analyzed. Finally, three spectra were recorded at $325^{\circ}C$, (Figure 3b) which was the final probe temperature for this sample. Weighing the sample before and after analysis showed that 94% of this material was volatilized.

These results illustrate the vast amount of information to be obtained by combining chemical separations with nonfragmenting FIMS in the analysis of coal liquefaction products.

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Figure 4 is an example of a spectrum of a crude oil analyzed by the computer in the same manner as the samples presented in Figures 2 and 3. The only difference was that the crude oil sample was "weathered" in the probe at room temperature to remove the most volatile constituents. The same sample was analyzed 5 times to assess the variance of the analytical procedure. Figure 5 presents the standard deviation of each of the mass peaks as a function of molecular weight. One can see here that the constituents below 250 amu have a high variance due to irreproducible preevaporation ("weathering") but in the mass range 250 to 550, the standard deviation is in the range of 3 to 6%, which is very satisfactory for such a complex analysis. It should be noted that even the most abundant constituents in our complex mixture amount to just about 0.6% of the total. At higher molecular weights, there is an increase in the variance predominantly because of the lower abundance of these constituents and possibly also because of some irreproducible pyrolysis or polymerization of such minor components. The effect of abundance on the variability of the individual constituents can be seen in Figure 6 which also presents the theoretical lower limit of variance due to statistical fluctuations of the ions counted. The two lines "200" and "800" designate the theoretical limit for these two extreme cases of molecular weights. The limits are different because of the difference in the monitoring time per amu during the magnetic scanning. The actual variance is about 2 to 3 times higher than the theoretical lower limit. This is fairly satisfactory in view of the complexity of the sample and the analytical procedure.

Field Desorption Experiments

Two years ago, we developed at SRI a novel type of field desorbing source that used a broken metal tip (11). We have also shown that ionic and other polar substances field desorb more readily when dissolved in an appropriate nonvolatile matrix. Our preliminary tests on low molecular weight hydrocarbon polymers were highly encouraging (9). Recently, we have extended our experiments, using broken graphite rods and bundles of graphite rods and bundles of graphite fibers as field desorbing sources, with evan greater success. We applied these sources to the analysis of asphaltenes. Figure 7 shows a field desorption spectrum (obtained on a multichannel analyzer) of the asphaltenes of SRC produced from Illinois No. 6 coal. The spectrum was obtained from a graphite fiber field desorbing bundle at 205°C.

An example of a computer handled FD spectrum of asphaltenes (produced from Kentucky coal) is presented in Fig. 8. In order to provide a direct comparison of the characteristics of FD and FI spectra currently available, Figures 8–12 show the raw data as it was acquired by the computer, rather than the normal bar-graphs. The resolution of the FD spectrum is inferior to that obtained by FI of the same sample (Fig. 9), probably due to the wider energy spread of the field desorbed ions, as well as to the fluctuating nature of the FD ion beam. Note, however, the significant mass peaks at about 395 amu in the FD spectrum which are absent in the FI spectrum. This feature appears again at somewhat higher temperatures (157-158°C) as shown in Figure 10. Figure 11 a–d present FD spectra in the temperature range 160 to 187°C. Comparison of these spectra with the FI spectrum over the same temperature range (Fig. 9) and over a higher temperature range (Fig. 12) shows that under FD, one ionizes the same constituents, or other compounds of comparable molecular weight, at significantly lower temperatures. The reproducibility and resolution obtained by FD are, however, major limiting factors in the application of

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this technique as a quantitative way to characterize coal products. Some of these limitations could be overcome by focal plane simultaneous ion collection techniques (e.g., photoplate mass spectrography).

Summary

We have shown that mass spectrometric multicomponent analysis techniques are ideal for the characterization of coal liquefaction and fuel products. These include the capability of determining molecular weight profiles up to 1000 amu with unit amu resolution and the ability to obtain and record molecular weight profiles as a function of sample temperature during a temperature programmed evaporation of the analyzed sample.

Combined with appropriate liquid chromatographic separation techniques or certain fast and quantitative derivatization procedures to separate coal liquefaction products into families of compounds, advanced FIMS offers an unprecedented, precise and meaningful analytical methodology for the characterization of coal products.

The field ionization technique described in this paper is not yet perfect, and it requires some further development in the areas of instrumentation, sample pretreatment, and data handling. However, there is sufficient evidence that this technique can provide the basis for one of the most comprehensive analytical methodologies ever available to coal research.

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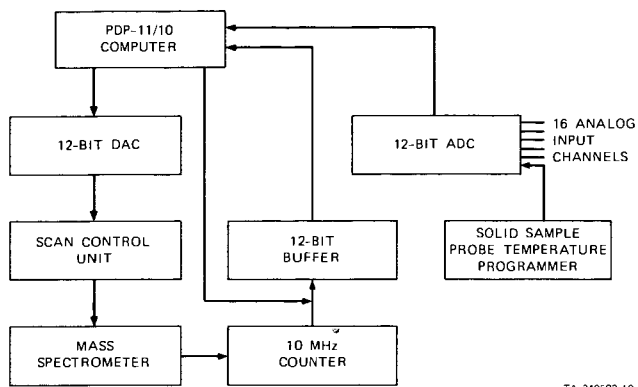
FIGURE 1   MASS SPECTROMETER-COMPUTER INTERFACE
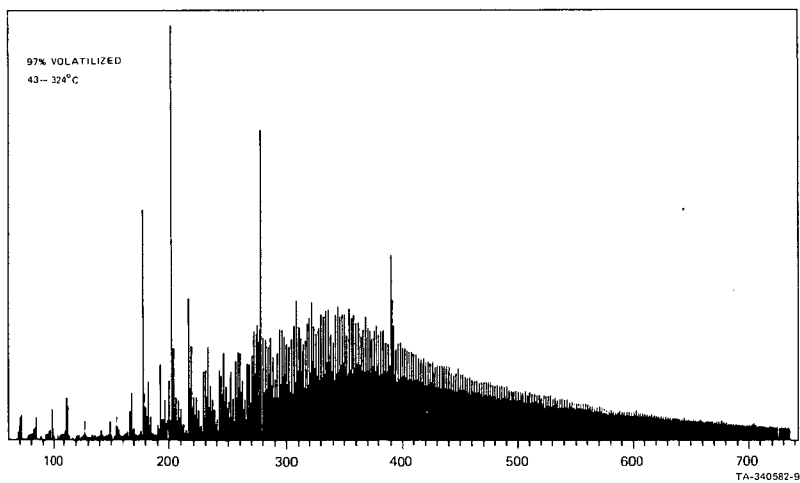
FIGURE 2   KENTUCKY 9/14 SRC, OILS FRACTION (SOURCE: ARCO)

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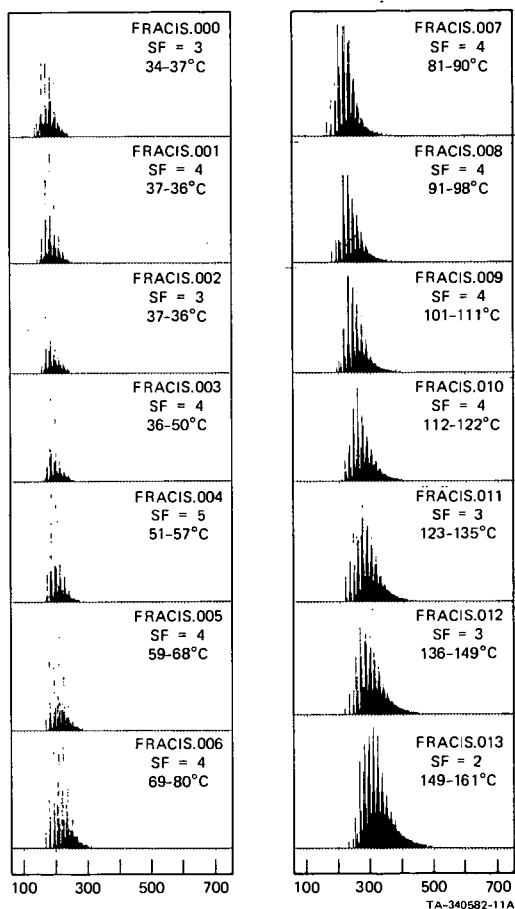
FIGURE 3A FRACTIONS 1 AND 2 FROM H-COAL PRODUCT 177-57-49 BY COLUMN
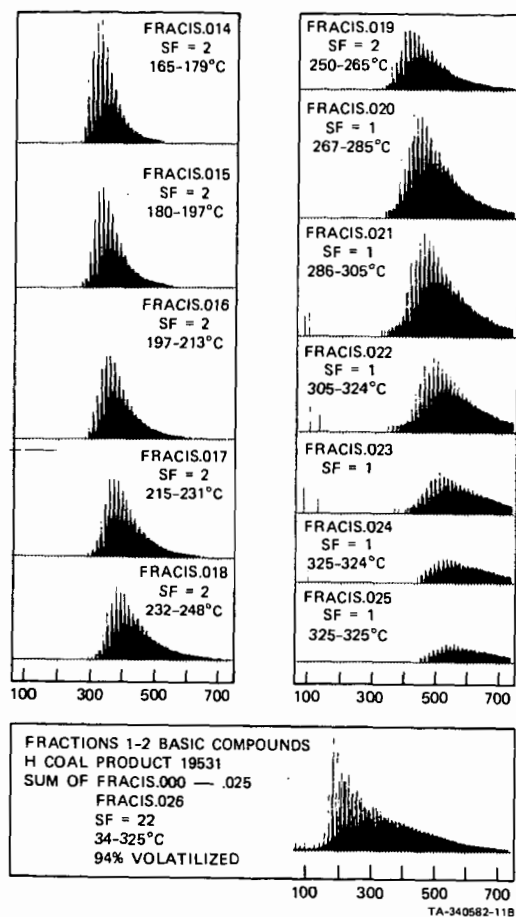CHROMATOGRAPHY (SOURCE: ARCO)

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FIGURE 3B FRACTIONS 1 AND 2 FROM H-COAL PRODUCT 177-57-49 BY COLUMN
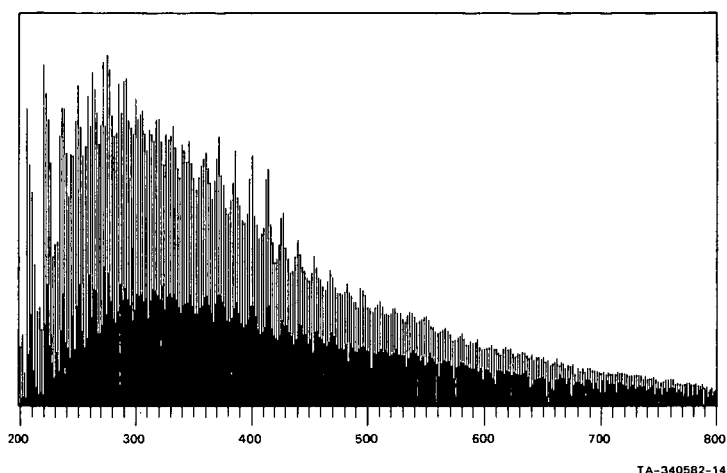CHROMATOGRAPHY (SOURCE: ARCO)

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TA-340582-14
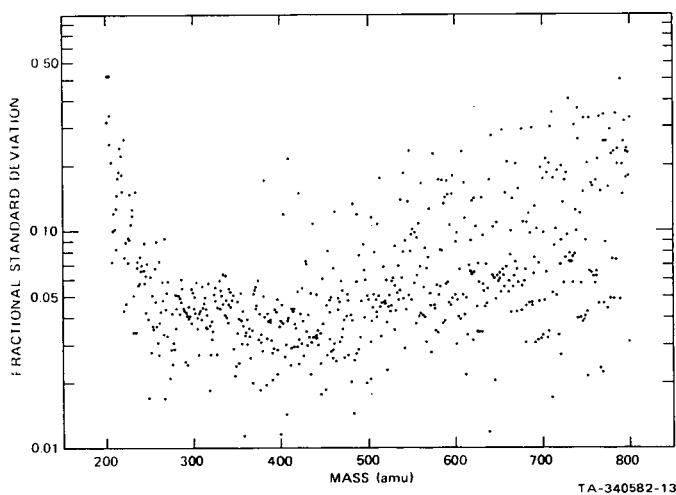
FIGURE 4   VENEZUELAN OIL WEATHERED IN MASS SPECTROMETER

TA-340582-13

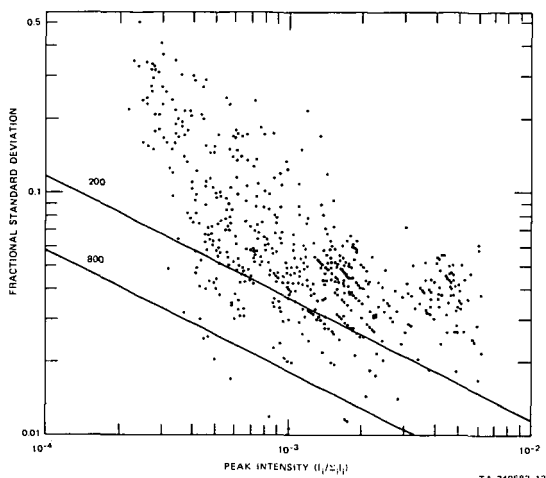FIGURE 5   STANDARD DEVIATION OF EACH OF THE MASS PEAKS AS FUNCTION
OF MOLECULAR WEIGHT

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FIGURE 6   EFFECT OF ABUNDANCE ON VARIABILITY OF INDIVIDUAL CONSTITUENTS
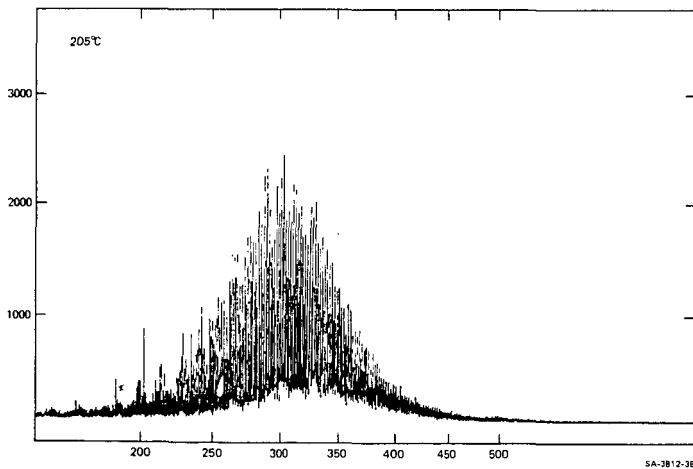
FIGURE 7   ASPHALTENES FROM ILLINOIS NO. 6 COAL, SRC PRODUCT, ARCO
            SAMPLE NO. 9634, GRAPHITE FIBERS SOURCE – FDMS

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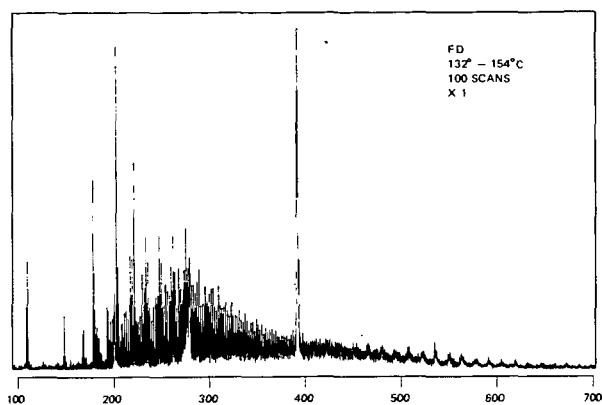
FIGURE 8   FIELD DESORPTION MASS SPECTRUM OF KENTUCKY SRC
            ASPHALTENES, 132°-154°C
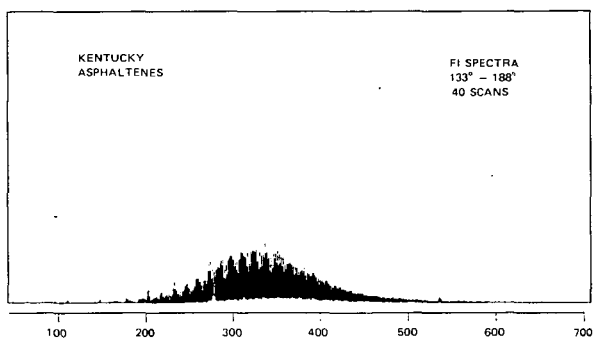
FIGURE 9   FIELD IONIZATION MASS SPECTRUM OF KENTUCKY
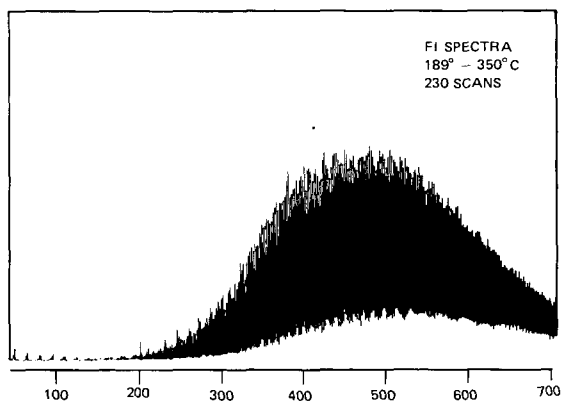   SRC ASPHALTENES, 133°-188°C
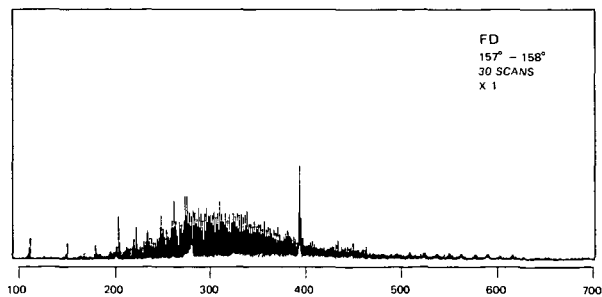
FIGURE 10   FIELD DESORPTION MASS SPECTRUM OF KENTUCKY
            SRC ASPHALTENES, 157°-158°C

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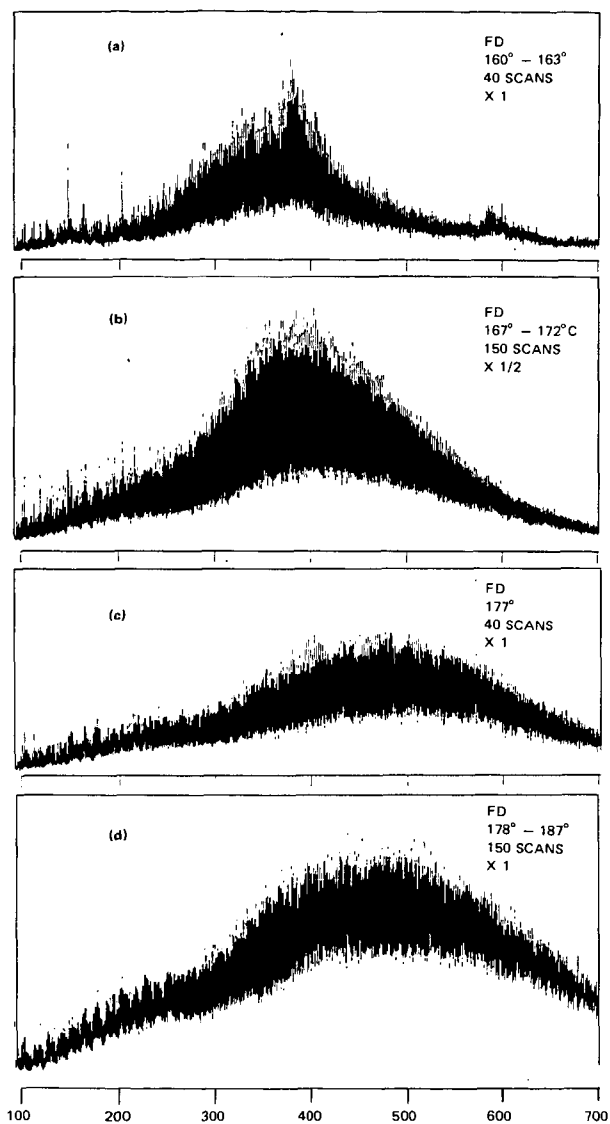
FIGURE 11   FIELD DESORPTION MASS SPECTRA OF KENTUCKY
SRC ASPHALTENES, 160°-187°C

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FIGURE 12   FIELD IONIZATION MASS SPECTRUM OF KENTUCKY
SRC ASPHALTENES, 189°-350°C

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OXIDATIVE DEGRADATION STUDIES OF COAL AND SOLVENT REFINED COAL

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INTRODUCTION

The bulk of the organic matter in coals consists of a macromolecular material of complex and variable composition. Many workers have attempted to degrade coals to smaller molecules which could be identified and interpreted in terms of coal structure. Oxidation has been one of the more important degradation methods. To date a number of oxidizing agents have been used. Among these were HNO_3, HNO_3-$K_2Cr_2O_7$, $KMnO_4$, O_2, H_2O_2-O_3 and NaOCl, all drastic oxidants. Because these reagents in general result in extensive ring degradations, with benzene carboxylic acids the only aromatic compounds identified, they have been of limited usefulness. Our approach has been to compare the products from drastic oxidants with more selective ones designed to break up the macromolecules into identifiable units with a minimum of chemical change so that units indigenous to coals can be identified. We have found aqueous $Na_2Cr_2O_7$ to be selective and have reported a number of polynuclear aromatic units which resulted from the dichromate oxidation of a bituminous coal and which we believe to be indigenous to the coal (1). We have explored a number of oxidizing agents using the samples listed in Table 1.

Table 1

Elemental Analyses of Samples (maf %)

No.	Sample	C	H	N	S	O (by diff)
1	Lignite (Sheridan Wyoming)	64.4	5.3	1.1	1.1	28.1
2	Bituminous (Illinois Seam #2)	77.8	5.4	1.4	2.1	13.3
3	Bituminous (Pittsburgh Seam #8)	82.7	5.5	1.3	2.8	7.7
4	Anthracite (Pennsylvania PSOC #85)	91.3	3.9	0.6	1.1	3.1
5	SRC (from Pittsburgh Seam #8)	87.2	5.5	1.8	1.2	4.3
6	SRC benzene-methanol ext.*	86.2	5.6	1.8	0.7	5.7
7	Char	84.9	1.7	---	---	---
8	Synthetic Polymer (from Fischer-Tropsch) (2)	80.0	5.1	1.3	0.0	13.6
9	Polymeric Material (from Murchison Meteorite (2))	76.1	4.6	2.8	1.3	15.2

*The SRC was fractionated into 3 fractions on the basis of solubility: hexane (4.5%), benzene-methanol mixture (82.3%), pyridine (11.8%) and a small residue (1.4%).

In addition to four coals, a solvent refined coal (SRC) and two completely abiotic samples, the synthetic Fischer-Tropsch polymer, and the polymer from the Murchison meteorite, were used for comparison and to test the oxidation methods.

RESULTS AND DISCUSSION

Identification of products: In general the products of oxidation were chiefly carboxylic acids which were esterified with diazomethane to increase their volatility for easier analysis by time-of-flight mass spectrometry (TOFMS), a variable temperature solid inlet, GC-TOFMS and high resolution mass spectrometer (HRMS).

Nitric Acid Oxidation: All samples of Table 1 except #6 were refluxed with 70% HNO_3 for 16-24 hours yielding a clear orange colored solution. The acid solutions were evaporated to dryness under reduced pressure and the residue weighed. The methylated acids were analyzed by GC-MS, HRMS and the solid probe. Fragmentation patterns and precise mass determination of both molecular ions and fragments, in particular $(M-OCH_3)^+$, were used for identification. In Figure 1 are summarized the data for benzene carboxylic acids (as their methyl ester). The synthetic sample had been prepared by heating CO, H_2 and NH_3 with an Fe-Ni catalyst at 200°C for six months (2). It was a macromolecular material insoluble in organic solvents, HCl, HF and KOH. Despite the drastic nature of the nitric acid oxidation it appears that useful information can be obtained by the procedure. For example the yield of total acids and the number of carboxylic acid groups per benzene ring seem correlated with the degree of condensation of the original material. The spectra from the synthetic sample from the Fischer-Tropsch reaction, and from char are relatively simple consisting primarily of the benzene carboxylic acid esters with from two to six ester groups. The coal samples and coal derived products (except for char) are more complex and contained nitro substituted esters and pyridine derivatives. Note the similarity between the synthetic sample and the char prepared from Illinois bituminous coal by heating under vacuum to 800°C. The abundance of the benzene hexacarboxylic acids for these two suggest a high degree of condensation in the original samples. The similarity in distribution of the oxidation products from the two bituminous coals (the Illinois and Pittsburgh) is striking. The solvent refined coal derived from the Pittsburgh #8 coal is shown later (Figure 3, Table 2) to have a higher degree of aromatic ring condensation than its feed coal. Thus it is surprising to see the shift to fewer acid groups for SRC. This may mean that many aliphatic crosslinks were destroyed in the SRC process and evolved as light hydrocarbons.

The results from the meteoritic polymer (not shown in Figure 1) were very similar to those of the synthetic polymer.

Sodium dichromate oxidation: In general 1-3 g of sample was heated at 250°C for 36-40 hours with excess $Na_2Cr_2O_7$ (60-120 ml of 0.4 $\underline{M}$ - 0.6 $\underline{M}$) with stirring. This procedure oxidizes side chains and alicylic appendages to polynuclear aromatic systems with a minimum of degradation of aromatic rings (3). We have found that model compounds are oxidized in high yields (78-95%)   to their corresponding carboxylic acids. Samples 1, 2, 3, 4, 6, and 9 were oxidized with $Na_2Cr_2O_7$ with a high degree of conversion to soluble or

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volatile compounds (70-100%). The yields of soluble compounds were 50-70%
of the weight of the original samples. The anthracite also yielded 17% of a
humic acid type material of high molecular weight soluble in alkaline solu-
tion. In Figure 2 are shown graphically the relative abundances of aromatic
and heteroaromatic units produced by the dichromate oxidation of three coals
(samples 1, 2 and 4). It is obvious that the degree of aromatic condensation
increases with rank of coal from lignite to bituminous to anthracite. The
$Na_2Cr_2O_7$-aq oxidation procedure has been questioned because of the possibility
that major structural rearrangement with pyrolytic formation of polynuclear
aromatic compounds might occur during the reaction at 250°C (4). The fact
that no polynuclear aromatic compounds with more than two fused rings were
detected in the oxidation products of lignite (sample 1) and that the degree
of condensation increases with rank of coal is internally consistent and
suggests that condensation during oxidation with $Na_2Cr_2O_7$ is minimal. In a
blank experiment bituminous coal (sample #2) which had been extracted with
an organic solvent to remove trapped compounds was heated at 250°C for 40
hours with water. An insoluble residue 96.2% and inorganic salts 2.9% were
obtained. Mass analysis of the residue was indistinguishable from that of
the original coal and the H/C ratio was unchanged. Furthermore, detailed
pyrolysis studies of the coal showed no evidence of significant thermal
decomposition until heated above 250°C.

    The gas chromatograms of the oxidation products (as methyl esters) from
the Pittsburgh coal (sample 3) and its SRC (benzene methanol extract-sample
6) are shown in Figure 3. The numbered peaks are identified·in Table 2. A
greater degree of aromatic condensation of the SRC extract over that of its
feed coal is observed. For example, naphthalene and phenanthrene rings are
much more abundant in the SRC. The dibenzofuran ring is the most abundant
heterocyclic to have survived the SRC process.

    Fifteen aromatic ring systems were identified in the $Na_2Cr_2O_7$ oxidation
product of the meteorite polymer: benzene, biphenyl, naphthalene, phenan-
threne, fluoranthene (or pyrene), chrysene, fluorenone, benzophenone,
anthraquinone, dibenzofuran, benzothiophene, dibenzothiophene, pyridine,
quinoline or isoquinoline and carbazole (2). These data support the
generally accepted idea that the polymeric material in meteorites has a
highly condensed aromatic structure (2, 5, 6) and gives us confidence in the
dichromate oxidation procedure.

    Photochemical oxidations: Oxidation by air bubbling through an aqueous
HCl solution while irradiating with ultraviolet light from a high pressure
mercury lamp was investigated. In Table 3 are shown the results obtained
with model compounds. From the results with the model compounds it appears
that aromatic hydrocarbons are readily oxidized to benzene carboxylic acids.
On the other hand N-heterocyclics resist oxidation. In Table 4 are listed
·the aromatic carboxylic acids isolated from a bituminous coal (sample 2)
after photochemical oxidation. The products from lignite (sample #1) were
primarily benzene carboxylic acids with only traces of pyridine tricarboxylic
acids and xanthone di- and tricarboxylic acids. Several aliphatic carboxylic
acids were identified (after methylation) in the photo-oxidation product of
bituminous by TOF variable temperature solid inlet and HRMS. They are
methyl esters of malonic acid, succinic acid, glutamic acid and saturated
monocarboxylic acids ($CH_3-(CH_2)_n-COOCH_3$ n = 1-7). The fragments for 3-methyl

Table 2

Aromatic Acids Found in the Oxidation
of SRC and Its Feed Coals[a] Identified as Methyl Esters

C Peak Number		Number of $-COOCH_3$	Relative Abundance ($\pm$ 15%)[b]	
			SRC Extract	Coal
1	Benzene	2	100	100
5		3	58	29
10		4	9	10
4	Biphenyl	1	3	9
2	Naphthalene	1	47	30
8		2	82	29
16		3	24	8
		4	*7*	*3*
13	Phenanthrene	1	82	28
20		2	8,*15*	*8*
		3	*5*	*7*
		4	*1*(T)	---
19	Pyrene/Fluoranthene	1	7	*3*
		2	*4*	*2*
11	Fluorenone	1	4	8
		2	*3*	*2*
		3	*3*	---
14	Anthraquinone	1	26	4
		2	*3*	---
7	Dibenzofuran	1	32	21
17		2	9	4
		3	*10*	*4*
15	Xanthone	1	4	9
		2	*6*	*7*
		3	*2*(T)	*3*
3	Benzothiophene	1	---	4
12	Dibenzothiophene	1	*2*	8
		2	---	5
	Pyridine	3	---	*5*(T)
	Carbazole	1	*4*	*3*
		2	*3*	*4*
18	Benzoquinoline/Acridine	1	3	7
		2	*5*	*4*
		3	*2*	*2*
6[c]				11
9[d]				22

Table 2 (Footnotes)

[a] 92% of the extract was oxidized and the yield of total acidic and non-acidic less volatile compounds was ≈59%. For the feed coal, 84% of the coal was oxidized; Yield of totals was ≈58%.

[b] Benzene dicarboxylic acid methyl ester is normalized to 100.

[c] Peak no. 6 is tentatively identified as trimethoxyxanthone.

[d] Peak no. 9 shows prominent mass ions at 216 and 215. HRMS shows their elemental composition corresponding to $C_{12}H_{10}O_3N$, $C_{12}H_9O_3N$ or $C_9H_{12}O_6$, $C_9H_{11}O_6$. Identification has not been made at this present time.

T = identification tentative; --- = not detected; x = peak consists of more than one component which are difficult to identify by GC-MS.

Italics indicate that identification and estimation of relative abundances were made by TOF variable temperature solid inlet and HRMS, because of difficulty of identification by GC-MS.

Table 3

Photochemical Oxidation of Model Compounds*

Compound	Unreacted[+] (%)	Major Oxidation Products [§]
p-cresol	0	unident. small species, polymer
anisole	0	unident. small species, polymer
naphthalene	8	phthalic acid
1,4-diMe-naphthalene	5	phthalic acid
2,6-diMe-naphthalene	7	benzene-1,2,4-tricarboxylic acid
indane	3	phthalic acid
fluorene	8	fluorenone
acenaphthene	10	phthalic, naphthalene-1,8-dicarboxylic acids
phenanthrene	24	phthalic acid, phenanthrene-9,10-diketone
pyrene	12	benzene tri- and tetracarboxylic acids
dibenzofuran	32	styrene, salicyclic acid
xanthone	78	unidentified chloro compounds
dibenzothiophene	43	styrene, thiophenol
carbazole	78	polymer
N-Et-carbazole	83	polymer
poly(2-vinylpyridine)	8	pyridine-2-carboxylic, pyridine-2-aldehyde,
-polystyrene polymer		benzoic, malonic, and succinic acids

*The oxidation was carried out in 10% aq. HCl solution for 6-10 days.
+Values are accurate to ±10%.
§After preliminary separation into acidic, neutral, and basic fractions, products were identified by TOFMS with variable temperature solid inlet. Except for the first two samples and the two carbazoles, all identifications were checked by high-resolution MS. For the italicized samples, GC-MS was used as well, after esterification of the product.
    All major products were accompanied by lesser amounts of their monochloro derivatives.

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Table 4

Aromatic Acids Found in the Photochemical Oxidation of Bituminous Coal: Identified as Methyl Esters[a,g,h]

Nucleus	Number of -COOCH$_3$	Precise mass (M-OCH$_3$)$^+$			Relative Abundance[b] ± 15-20%
		elemental composition	observed	Dev. x 10^3	
Benzene	2	C$_9$H$_7$O$_3$	163.0388	-0.7	42
	3	C$_{11}$H$_9$O$_5$	221.0457	0.8	100
	4	C$_{13}$H$_{11}$O$_7$	279.0510	0.6	97
	5	C$_{15}$H$_{13}$O$_9$	337.0555	-0.3	29
	6	C$_{17}$H$_{15}$O$_{11}$	395.0593	-2.0	4
Cl-benzene[c]	2	C$_9$H$_6$O$_3$Cl	196.9990	-1.5	24
	3	C$_{11}$H$_8$O$_5$Cl	255.0066	0.6	31
	4	C$_{13}$H$_{10}$O$_7$Cl	313.0125	1.1	26
	5	C$_{15}$H$_{12}$O$_9$Cl	371.0124	-4.4	2
Fluorenone	2	C$_{16}$H$_9$O$_4$	265.0494	-0.6	9
Anthraquinone	2	C$_{17}$H$_9$O$_5$	293.0451	0.2	3
	3	C$_{19}$H$_{11}$O$_7$	351.0520	1.6	1
Phthalan	2 (T)	C$_{11}$H$_9$O$_4$	205.0478	-2.2	2
	3 (T)	C$_{13}$H$_{11}$O$_6$	263.0572	1.8	1
Xanthone	2	C$_{16}$H$_9$O$_5$	281.0461	1.2	9
	3	C$_{18}$H$_{11}$O$_7$	339.0510	0.6	7
Dibenzofuran[d] and/or naphthofuran	2	C$_{15}$H$_9$O$_4$	253.0477	-2.3	3
	3	C$_{17}$H$_{11}$O$_6$	311.0560	0.6	2
Pyridine	2	C$_8$H$_5$O$_3$NCl[e]	197.9974	1.6	3
	3	C$_{10}$H$_8$O$_5$N	222.0408	0.5	3
	4	C$_{12}$H$_{10}$O$_7$N	280.0488	3.2	3.5
Quinoline and/or isoquinoline	1	C$_{10}$H$_6$ON	156.0412	-3.7	0.5
	2	C$_{12}$H$_8$O$_3$N	214.0468	-3.5	2
Carbazole[f]	1	C$_{13}$H$_8$ON	194.0598	-0.7	4
	2	C$_{15}$H$_{10}$O$_3$N	252.0660	-0.0	2
	3	C$_{17}$H$_{12}$O$_5$N	310.0708	-0.6	2
Acridone	1	C$_{14}$H$_8$O$_2$N	222.0525	-2.9	5
	2	C$_{16}$H$_{10}$O$_4$N	280.0592	-1.8	2
	3	C$_{18}$H$_{12}$O$_6$N	338.0635	-2.8	1

Table 4. Footnotes

[a] Some preliminary results were reported earlier (1). Identification based on TOF variable temperature solid inlet, GC (Carbowax 20 $\underline{M}$)-TOFMS and high resolution MS.

[b] Benzene tricarboxylic acid methyl ester is normalized to 100. Relative abundances were estimated from the GC and an integration of the base peak of each compound during the time that the sample was completely volatilized in the MS.

[c] Monochlorobenzene carboxylic acids were always obtained when coal or model compounds were oxidized in 10% HCl aq. solution. Chlorocarboxylic acids of other aromatics were also observed in very low yield.

[d] Relatively large amounts of dibenzofurans were found to be produced by $Na_2Cr_2O_7$-oxidation (1), while photo-oxidation produced dibenzofuran carboxylic acids in low yield. Perhaps this shows the photochemical procedure destroyed most of the dibenzofuran ring.

[e] For pyridine dicarboxylic acid, only chloroderivatives were found.

[f] The previous estimates of relative abundances (1) were somewhat high.

[g] The products of lignite photo-oxidation in 5% KOH aq. solution were very similar to those shown in this Table. In addition some mono- and dimethyl-benzene carboxylic acids were identified.

[h] Polynuclear aromatic carboxylic acids such as naphthalene and phenanthrene found in the $Na_2Cr_2O_7$ oxidation product (see Fig. 2) are not observed in this product. From our model experiments, we have found that these aromatic compounds are oxidized by the present procedure.
T = identification tentative.

and 3,3-dimethyl aliphatic carboxylic acid methyl esters were also seen in the mass spectra. A similar observation was made for the oxidation product of lignite.

Hydrogen Peroxide-Acetic Acid: It is probable that in the oxidation experiments described above aromatic units with phenolic groups would have been destroyed. Schnitzer et al. (7) have shown that an acetic acid-H_2O_2 mixture under mild conditions oxidizes humic acids while preserving phenols. Using this procedure we have oxidized lignite (sample #1) and bituminous coal (sample #2) with over 80% conversion to methanol soluble acids and have methylated the acids produced.

The gas chromatogram of the aromatic portion of the methylated product from lignite is shown in Figure 4. The identification of individual compounds was made by coincident MS and HRMS of the mixture. The methyl esters identified gave the following approximate distribution: 36.1% benzene, 7.6% methyl-benzene, 22.1% methoxy-benzene, 15.9% furan and 18.2% dibasic aliphatic. For the bituminous coal the methoxy derivatives were half as abundant. These results suggest that the lignite has twice the phenolic content of the bituminous coal. It is interesting to note that methyl furan

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tetracarboxylate has been identified and other furan derivatives have been tentatively identified.

It appears that the coals are acting as catalysts for this oxidation. If 2,6-dimethylnaphthalene is reacted with H_2O_2 under the same conditions as used for the coals, only 2,6-dimethylnaphthaquinone is isolated in essentially quantitative yield. With the addition of a small amount of lignite to the reaction, 5-methyl phthalic acid is obtained as the major product. Also no hydroxylated benzene carboxylic acids were isolated which indicates that this procedure does not hydroxylate aromatic rings. Transition metals are known to catalyze reactions of hydrogen peroxide. Part of the catalytic effect may be due to the mineral matter in the coal.

No polyhydroxyl benzene carboxylic acids have been observed in the products from either coal. It is expected that these species would undergo ring oxidation and subsequent degradation. However, the concentration in coal of these species is probably small. These compounds are expected to be very reactive and probably would not survive the coalification process. We have examined aqueous NaOH extract of the Wyoming lignite. Numerous hydroxylated aromatic hydrocarbons and aromatic acids were identified, but no polyhydroxylated species were detected.

Sodium Hypochlorite Oxidation: On the basis of results of oxidation of coal with NaOCl, Chakrabartty et al. have suggested that coal has a non-aromatic "tricycloalkane or polyamantane" structure (8). They pointed out that no evidence for aromatic compounds other than benzene derivatives was found in their oxidation product. The specificity of NaOCl as an oxidant has been questioned (9) and is still in dispute (10). We are attempting to resolve the question and have oxidized samples 6, 9, and 2,6-dimethyl naphthalene under conditions described by Chakrabartty et al. (8, 10, 11). Of particular interest is the oxidation of the polymeric material from the Murchison meteorite (sample 9). Numerous studies have shown this material to be a highly condensed aromatic structure. All samples were nitrated according to the method of Chakrabartty et al. When nitration was followed by NaOCl oxidation at 60°C for 3-4 hours almost no oxidation was observed for nitrated samples 6 (SRC) or 9 (meteorite) while 26% of nitrated dimethyl naphthalene was converted to benzene carboxylic acids and their nitro and/or methyl derivatives. No naphthalene acids were detected. When the reaction was continued for 15 hours, at 65-70°C 57% of sample 9 and 42% of sample 6 were oxidized to water soluble acids. Polynuclear aromatic and heterocyclic acids were not detected in the oxidation products of either sample although both are highly aromatic. Benzene carboxylic acids were the major products (nitro and/or methyl derivatives and a methyl chloro dicarboxylic acid). Apparently polynuclear aromatic systems were destroyed and the product distribution closely resembled that from a nitric acid oxidation. Obviously more work is needed to clarify the role of NaOCl in the oxidation of coal.

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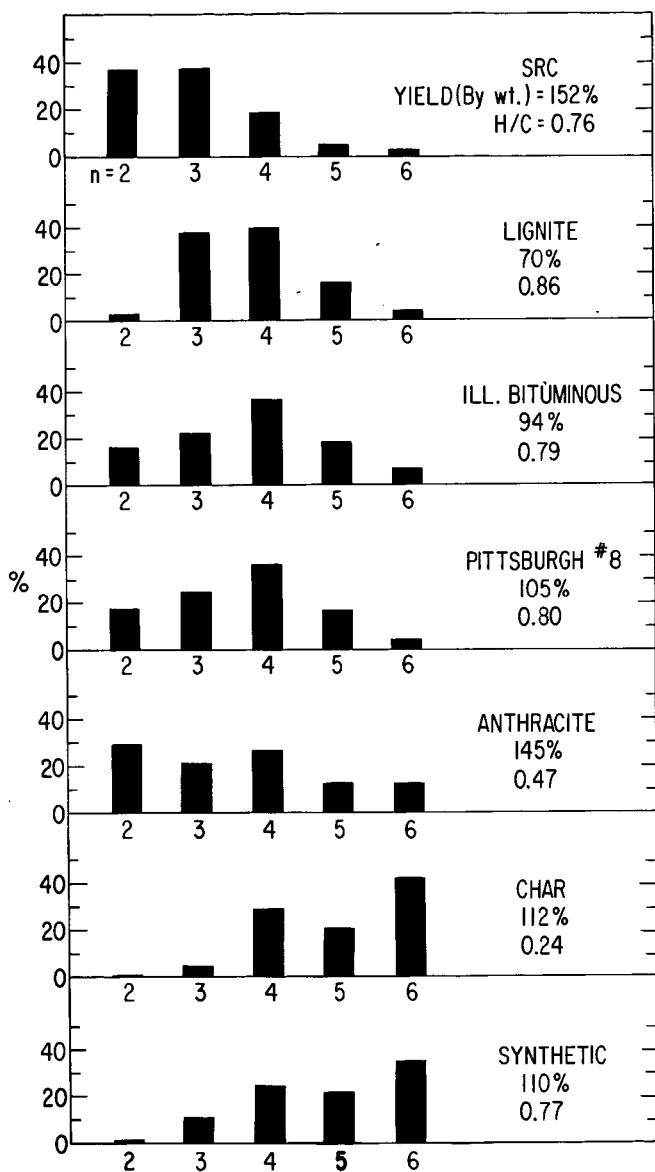(11) S. K. Chakrabartty and H. O. Kretschmer, J. Chem. Soc. Perkin 1, 222 (1974).

Figure 1. Abundances (%) of benzene carboxylic acids, determined as their methyl esters, produced by nitric acid oxidation. n = number of $(COOCH_3)$ groups per benzene ring.
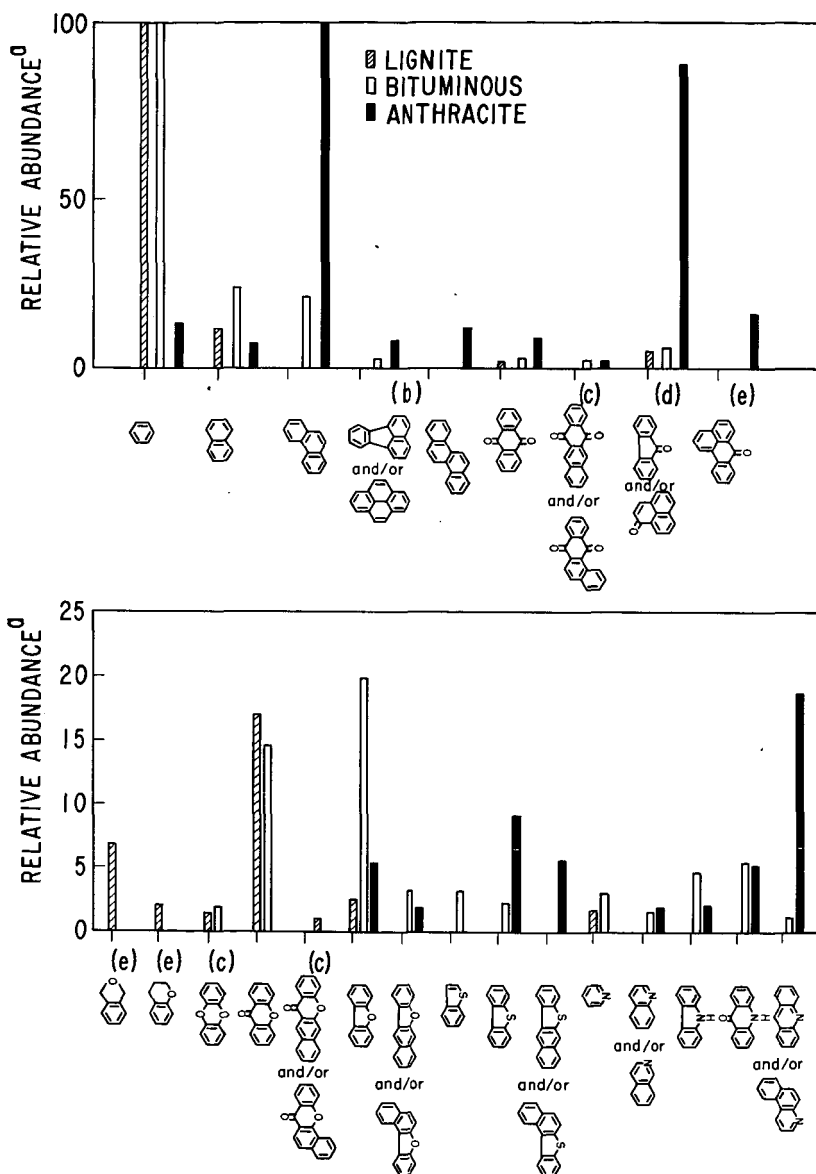
Figure 2. Relative abundances of aromatic and heteroaromatic units produced by sodium dichromate oxidation of lignite, bituminous and anthracite coals.
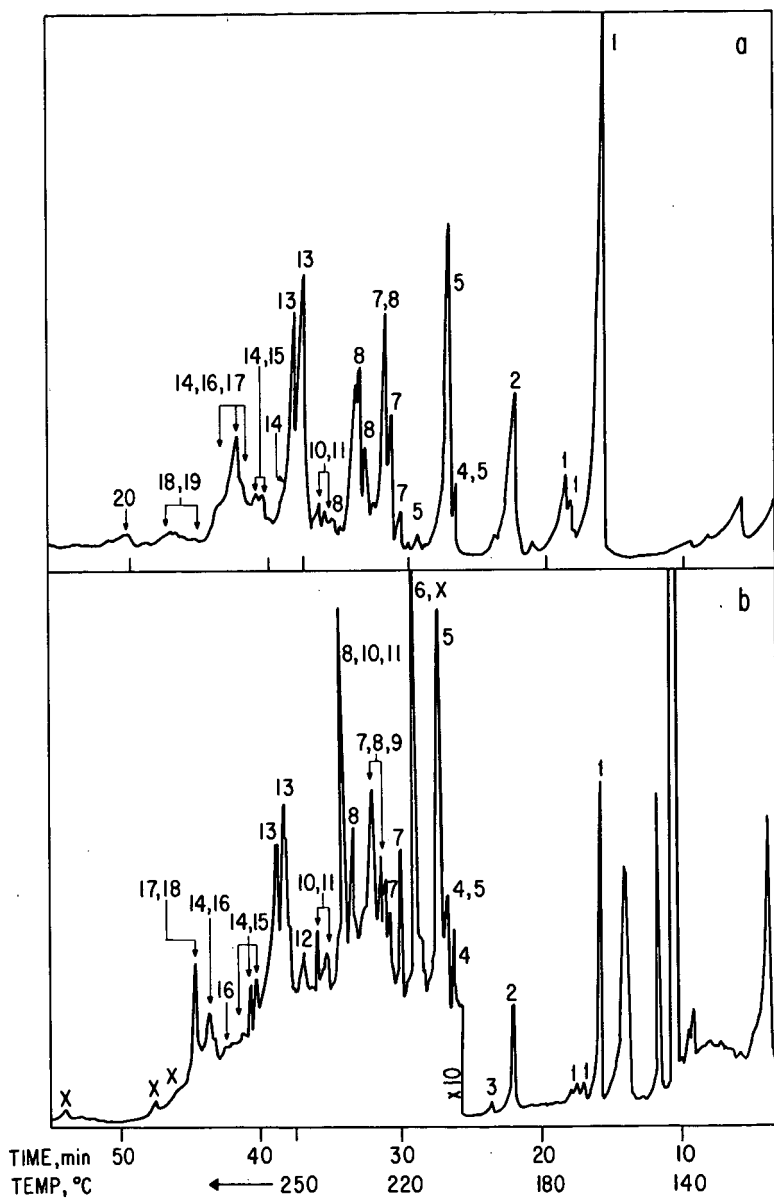
Figure 3. Gas chromatograms of methylated $Na_2Cr_2O_7$ oxidation products of SRC benzene-methanol extract (a) and its feed coal, Pittsburgh #8 (b). Separations were made on an OV-101 SCOT column.
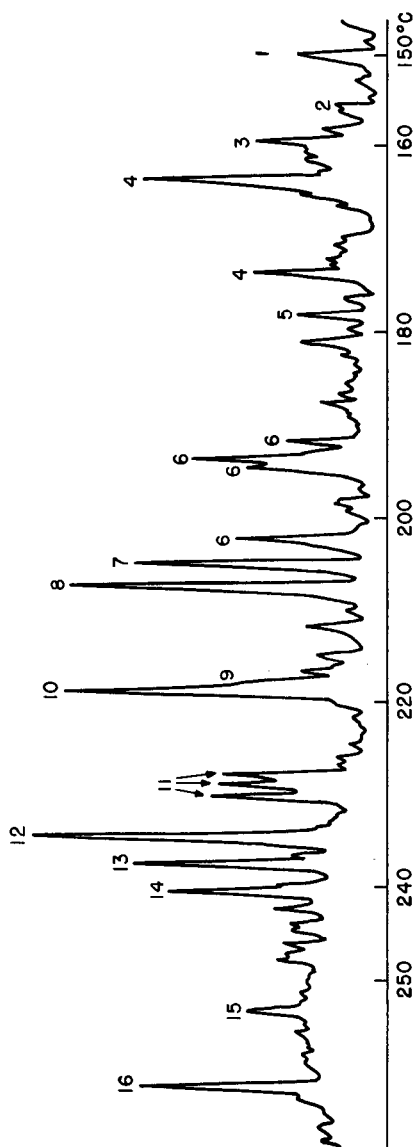
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Figure 4. Methyl esters from hydrogen peroxide-acetic acid oxidation of lignite separated on an OV-101 SCOT column. Numbered compounds: 1. methyl o-methoxybenzoate; 2. methyl m- or p-methoxybenzoate; 3. methyl methylfurandicarboxylate; 4. methyl benzenedicarboxylate; 5. methyl carbomethoxyphenylacetate; 6. methyl methoxybenzenedicarboxylate; 7. methyl 1,2,3-benzenetricarboxylate; 8. methyl 1,2,4-benzenetricarboxylate; 9. methyl methoxybenzenetricarboxylate; 10. methyl furantetracarboxylate; 11. methyl methoxybenzenetri- carboxylate; 12. methyl 1,2,3,4-benzenetetracarboxylate; 13. methyl 1,2,4,5-benzenetetracarboxylate; 14. methyl 1,3,4,5-benzenetetracarboxylate; 15. methyl methoxybenzenetetracarboxylate; and 16. methyl benzenepentacarboxylate.

PHENOLS AS CHEMICAL FOSSILS IN COALS

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Introduction

It is generally considered that vitrinite, the principal maceral in most coals, represents coalified, partly decayed wood. Hence lignin should be one of the important precursors to the vitrinites in coals. Accordingly, it would be interesting to know whether any chemical fossils related to lignin could be found in coals. The purpose of this paper is to report what we believe to be a successful search for such fossils. The experimental approach exploited a degradation reaction developed in a study of soil humic acids by Burges et al.[1]

This reaction involves a reduction degradation with sodium amalgam and hot water. Thin layer chromatography of the ether soluble part of the product (yield, about 20%) showed the presence of a number of phenols and phenolic acids, most of whose structures bore obvious relationships to known microbial and chemical degradation products of lignin (I) but some to the A ring of fla- vonoids (II).
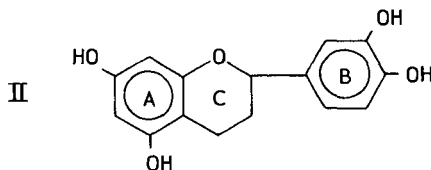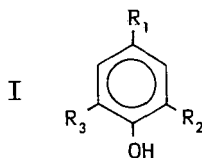
where R_1 = COOH, CHO, -CH=CH-COOH, -CH-CO-COOH, etc.; R_2 = H or OCH₃ or OH; R_3 = H or OCH₃ or OH. The R_1 group may represent a side chain of 1, 2 (rarely) or 3 carbon atoms, in various states of oxidation. Burges et al. therefore concluded that the humic acids they studied were condensates of phenolic com- pounds from the degradation of plant products with amino acids (see also Flaig[2]).

Humic acids can be extracted from peats and lignites but not from bitum- inous coals. However, oxidation of bituminous coals with aqueous performic acid generates in high yield (80-110% by weight) materials that closely resemble humic acids[3]. In preliminary studies performed some years ago by one of us (J.B.) while on leave of absence from his Institute, the Burges reductive degradation was applied to humic acids extracted from some peats and lignites, and produced by oxidation of a number of bituminous coals. A number of identifications of products were made by gas chromatography with co-injection of standards, but at that time facilities were only rarely available to permit confirmation by mass spectrometry. Such confirmation has been more fully obtained recently by another of the authors (S.R.), who also studied a wider range of coals (to- talling 43 samples).

It is proposed in this preliminary publication to describe the experimental procedures and to give a sufficient selection of the data to show what was found by co-injection and later confirmed by mass spectrometry.

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The major coal measures of the United States were laid down either in the Carboniferous era (ca. 300 m. years B.P.), or in the Cretaceous and Tertiary (130-60 m. years B.P.). Between these two eras a great deal of evolution occurred in the plant kingdom; associated with this were some changes in the nature of groups R_2 and R_3 in structure I above. However, having stated the fact, we need not pursue this matter here.

Experimental

Humic acids were extracted from peats and lignites with 0.5N sodium hydroxide following standard procedures.

The oxidation of coals with aqueous performic acid is highly exothermic. Five gm of coal was dispersed in 50 ml of anhydrous formic acid, and 50 ml of 30% hydrogen peroxide was added in 2 ml portions at such a rate that the temperature did not exceed 55°C (however, in the earlier phase, the coal/formic acid suspension was cooled in ice during the addition of H_2O_2). The mixture was then allowed to stand at room temperature with stirring for 24 hours. The washed and dried solid product was extracted with 1N NaOH under nitrogen and centrifuged. The extract was precipitated by acidification to pH 1. The washed and dried humic acids were redissolved in alkali and, following the procedure of Burges et al.[1], treated with 3% sodium amalgam while the solution was heated in an oil bath at 110-115° for 4-5 hours.

After removal of mercury, the resulting solution was acidified to pH 1 and centrifuged; the supernatant was carefully removed and the residue extracted twice by centrifugation with ether and twice with methylene chloride. Solvents were removed and the residues mixed. The residues were treated with Sylol HTP reagent (Supelco, Inc., Bellefonte, Pa.) under the conditions recommended for converting phenols to trimethylsilyl ethers and carboxylic acids to the corresponding esters.

Experiment showed OV 101 column packing (3% on 80/100 mesh Supelcoport) to be the most effective for gas chromatography of the six packings tested. GC analyses, with and without co-injection of standards, were performed with a Hewlett-Packard No. 5750 instrument, equipped with flame ionization detectors. GC/MS analyses in the later phase were made by Mr. David M. Hindenlang, using a Finnegan model 3000 instrument under the charge of Dr. Larry Hendry of the Chemistry Department of this University. OV 101 columns were again used. The GC/MS instrument was provided with a data system, and this was used to subtract the mass spectrum at the foot of each peak just before it began to elute, or just after it had done so, from the spectrum recorded as the maximum of the peak was eluted. Such a procedure is certainly arbitrary, but disc space could not be monopolized for continued storage of our data while other procedures were tested and interpretations worked out. Consequently, the raw MS data, massaged as described above, were reported for standards and unknowns as printouts tabulating m/e values and relative intensities, and comparisons were made by visual inspection of the printed data.

Results

On the dry basis the weight of crude oxidized coal was usually 85-105% of the weight of raw coal. The yields of daf humic acids were in the range 65-90% of dmmf coal. Within the range of rank studied (78-87% C dmmf), the yield tended to increase with increasing rank. Petrographic studies of the

oxidized products of three coals (by Dr. Alan Davis and Mr. Harrey Zeiss, to whom we are indebted) showed that the vitrinites were greatly altered compared with their appearance in the raw coals, while sporinite and the inert macerals had changed little or not at all. These apparently unaltered macerals could still be recognized in the NaOH-insoluble materials. Thus the humic acids were derived very largely from the vitrinitic macerals. The yields of ether soluble products from the reductive degradation were in the range 10-40% of the weight of humic acids taken; yields when the reaction is applied to soil humic acids were about 20%.[1] Yields from humic acids from the younger Western coals tended to be somewhat higher than those from Carboniferous coals of the eastern U.S.

Chromatograms obtained in the earlier phase of the work are shown in Figures 1 and 2, where the names of compounds identified, mostly by co-injection, are entered against the corresponding peaks (trivial names are used in the figures because they are usually shorter; a list of equivalent systematic names is given in the Appendix. Comparison of the structures with I and II above will show which may be biologically related). It will be seen that resolution is moderately good but that even so a number of major peaks are unidentified.

These curves are typical of what was found for products from the six coals studied. All 3 dihydroxy-benzenes were commonly found and 2 of the trihydroxy-benzenes. 2,6-Xylenol was frequently found in both the earlier and later work, and was the only one of the six xylenols to be identified. Several of the compounds frequently encountered (vanillin and vanillic acid, syringic aldehyde and acid, p. hydroxy-benzoic acid) are well known as degradation products of lignin. A peak is seen in Figure 1 labelled 2,5-dihydroxy-benzoic acid (2,5-DHBA), and another labelled 2,4-, 3,4-, 3,5-dihydro-xy-benzoic acid. Experiments with known compounds showed that the latter three isomers could not be resolved under the conditions used. Later work, using GC/MS, showed that of the three only the 3,4-isomer was in fact present, and this is lignin-related. However, the 2,5-isomer is not, though it could be derived from the A ring of flavonoids, 2,3,4-Trihydroxy-benzoic acid has no obvious biological associations, though the 3,4,5-isomer (gallic acid) occurs widely in the plant kingdom (both isomers were identified).

When, later, a wider range of samples was studied (with somewhat more severe conditions of oxidation), some very poorly resolved chromatograms were obtained; the products evidently often represent very complex mixtures of substances. Surprisingly, the products from nearly all of the younger western coals were resolved poorly or very poorly, while the resolution of those from the Interior and Eastern provinces ranged from mediocre to good. Representative examples of each type are shown in Figures 3 and 4. The resolution in Figure 3 is so bad that one might question whether any identifications are possible. In Table 1, we have assembled details of the mass spectra of four substances alleged to be identified from the GC/MS run shown in Figure 3, with details of the spectra of the standards. The agreement is surprisingly good, and the identifications are, taken with matching of retention times, reasonably secure. When resolution is better, as in Figure 4, one can surely be confident in the identifications; examples of the correspondence of mass spectral data are shown in Table 2.

It should be added that even when the GC/MS system is used, many promi-
nent peaks remain unidentified. However, many of these showed fragments of
m/e=73 in the corresponding mass spectra, so that they evidently contained
the trimethylsilyl group and were therefore phenols or acids or both.

In considering the origin of the substances shown as identified in
Figures 1-4, one must assume with bituminous coals that carboxylic acid groups
result entirely from the performic acid oxidation. There is every reason to
suppose that some of the hydroxyl groups were present as such in the raw coals,
but one must necessarily enquire to what extent is new OH introduced by the
oxidation (performic acid is a known reagent for converting alkenes to epox-
ides and cleaving them; this process occurs by a concerted electrophilic
mechanism. However, the mechanism of attack on coals could be quite dif-
ferent and might, for example, follow a free radical mechanism).

The substances named in Figures 1-4 can be arbitrarily classified as
follows: (1) "non-committal" substances - those like phenol, p. cresol and
benzoic acid, whose structures are relatively simple and contain no obvious
clues to origin, (2) those whose structures could obviously be related to
biological precursors, such as vanillic, syringic, ferulic and other substi-
tuted cinnamic acids, (3) those whose structures are relatively complex but
do not display any obvious association with biological precursors, such as
the dimethyldihydroxybenzene shown in Figure 1 (isomers not identified). Of
these classes, (1) requires no further comment here, while (3) presumably
may include - or consist largely of - compounds whose OH groups are an arte-
fact of the oxidation process. This leaves open the question, to what extent
are the compounds of class (2) chemical fossils or artefacts?

Many of the substances identified have methoxyl groups in the 3-position
or the 3,5-positions, as in lignins. These groups could hardly have been
introduced by the performic acid oxidation, and therefore indicate a chemical
fossil status for the substances. On the other hand, Blom et al.[4] state that
methoxyl groups are eliminated by metamorphism in the subbituminous range. We
must admit that the structures we identify as methyl phenyl ethers represent
a small weight fraction of the whole coals: but can also point out that Blom
et al. present no evidence that the Zeisel procedure, which they used in their
analyses, was completely effective (the reagent HI may not have penetrated
the pore structure fully), or even that it produced with coals the results
found with simple compounds. Whatever the mechanism of the performic acid
oxidation with coals, one would expect that if it introduces new OH groups,
more than one isomer would usually be produced. Therefore, where a peak in
the chromatograms was identified as due to a lignin-related substance like
vanillin or caffeic acid, the mass spectra corresponding to neighboring chro-
matographic peaks were carefully examined to determine whether they could
represent spectra of position isomers. Such isomers were rarely detected.
On the other hand, some of the relatively complex substances not obviously
related to biological precursors evidently did have isomers present.

We conclude that some of the OH groups in the products may well have
been introduced by the performic acid oxidation, but that most of the substances
of structure related to lignins were probably not artefacts.

The question, to what extent do the findings reported here relate to the
composition of whole coals, must be left for discussion in a later paper when
a more complete set of data can be presented. In concluding this paper, we

should draw attention to some implications of the findings, if the provisional assumption can be made that the findings do indeed have relevance to the structure of vitrinite macerals in coals:

1. o-Dihydroxybenzenes, and still more trihydroxybenzenes, are notoriously easily oxidized. This, if such structures are indeed present in vitrinites, we could explain why it is so difficult to nitrate or sulfonate coals, even with mild reagents, without accompanying oxidation[3], and also why coals so readily oxidize in weathering. Partially methylated polyphenols are less reactive, but still quite readily susceptible to oxidation.

2. *Ortho* - dihydroxybenzene derivatives are capable of chelating boron and other elements. Less information is available about o.hydroxy-methoxy derivatives, but there seems no reason why they should not be capable of chelation.

3. During catalytic hydrogenation of coals of any rank to liquid fuels, under conditions that give high conversion, a substantial fraction of the oxygen is removed. However, in interactions of coal with hydrogen donor solvent alone, or in applications of the SRC process, oxygen removal is less complete and the products may retain o.dihydroxybenzene structures, a point perhaps worthy of note by those concerned with the composition of coal liquids.

It is worth noting here that in a study of the products of laser pyrolysis of coals in the ionization chamber of a time-of-flight mass spectrometer, homologous series of what appeared to be dihydroxybenzenes were noted[5]. The technique could not distinguish positional isomers, but the finding is suggestive when taken with the data in this paper.

Acknowledgements

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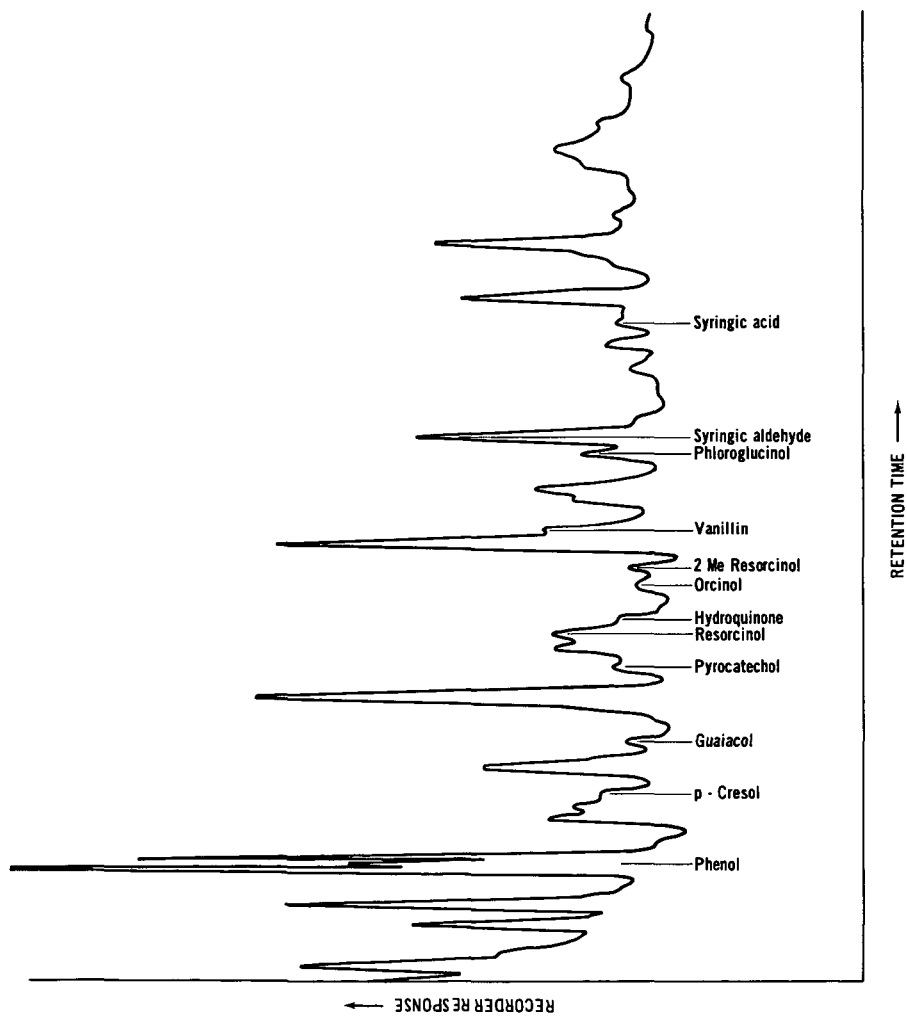
Figure 1. CHROMATOGRAM OF DEGRADATION PRODUCTS (AS TMS DERIVATIVES) FROM C SEAM COAL, BENHAM, KENTUCKY (HVA, PSOC 13)
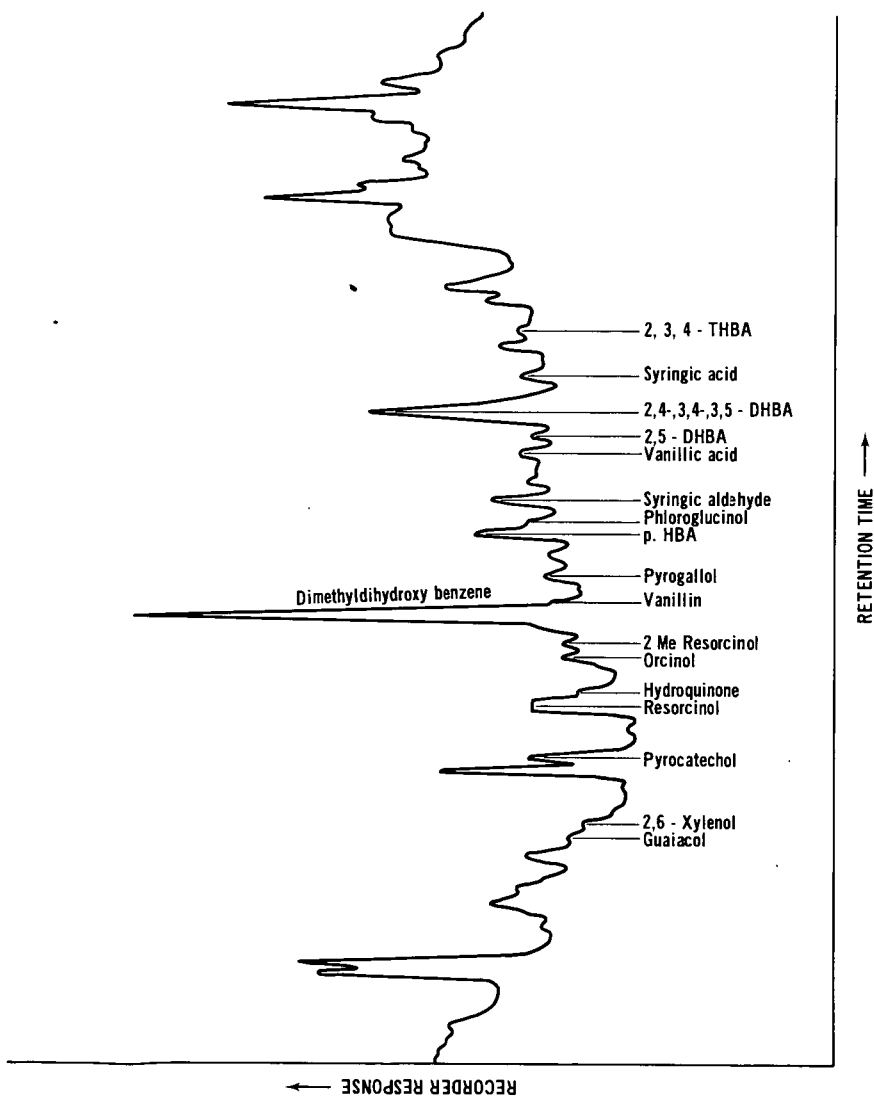
174

Figure 2. CHROMATOGRAM OF DEGRADATION PRODUCTS (AS TMS DERIVATIVES) FROM WYODAK SEAM COAL, GILLETTE, WYOMING (sbb., PSOC 100)
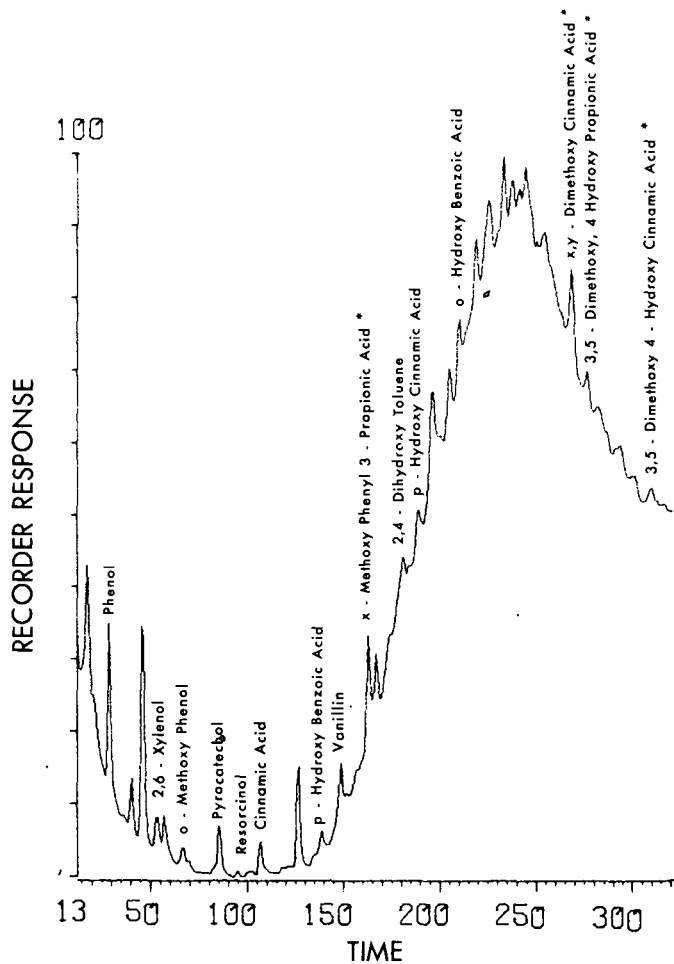
175

Figure 3. TOTAL ION CURRENT CHROMATOGRAM OF DEGRADATION PRODUCTS (AS TMS DERIVATIVES) FROM RED SEAM (HVC), KAYENTA, ARIZONA (PSOC 312)
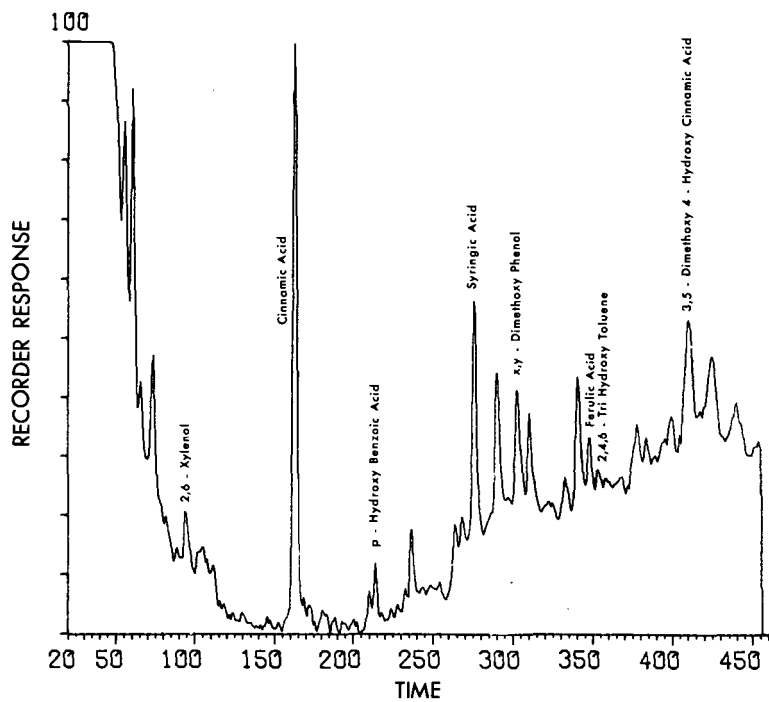
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Figure 4.   TOTAL ION CURRENT CHROMATOGRAM OF DEGRADATION PRODUCTS (AS TMS DERIVATIVES) FROM OHIO NO. 1 SEAM (HVC), JACKSON, OHIO (PSOC 202)

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Table 1

Data for MS Identification of Substances in Degradation Products of Coal from Black Mesa, Arizona (HVC)(PSOC 312)

Cinnamic Acid			p. Hydroxybenzoic acid		
m/e	Standard	Unknown	m/e	Standard	Unknown
p/p+1	3.98	4.13	p/p+1	3.28	2.73
205	100	100	73	100	100
57	82	86	193	45	63
45	48	39	267	44	59
145	27	23	223	42	56
55	25	20	45	21	41
89	20	16	75	15	23
67	18	14	126	13	17

Vanillin			p. Hydroxycinnamic acid		
m/e	Standard	Unknown	m/e	Standard	Unknown
p/p+1	6.95	5.15	p/p+1	6.00	5.27
194	100	. 88	13	100	83
23	83	100	219	76	100
193	53	45	235	61	79
209	37	60	293	32	41
151	29	38	191	21	39
45	27	33	45	16	25
165	9	17	75	15	19

Table 2

Data for MS Identification of Substances in Degradation Products of Coal from Ohio No. 1 Seam (HVC)(PSOC 202)

p. Hydroxybenzoic acid			Syringic acid		
m/e	Standard	Unknown	m/e	Standard	Unknown
p/p+1	3.28	3.18	p/p+1	3.72	3.15
73	100	100	73	100	100
193	45	52	45	18	29
267	44	48	141	15	23
223	42	41	327	12	19
45	21	34	312	10	13
75	15	19	89	10	15
126	13	14	297	9	10

Ferulic acid		
m/e	Standard	Unknown
p/p+1	2.71	2.93
73	100	100
75	48	49
117	38	35
225	24	32
181	22	30
129	22	25
297	20	31

Appendix. Trivial and Systematic Names of Relevant Phenolic Substances

resorcinol   1,3-dihydroxybenzene

pyrocatechol   1,2-dihydroxybenzene

phloroglucinol   1,3,5-trihydroxybenzene

pyrogallol   1,2,3-trihydroxybenzene

orcinol   3,5-dihydroxytoluene

2-methyl resorcinol 2,6-dihydroxytoluene

guaiacol   2-methoxyphenol

vanillin   3-methoxy-4-hydroxybenzaldehyde

vanillic acid   3-methoxy-4-hydroxybenzoic acid

syringic acid   3,5-dimethoxy-4-hydroxybenzoic acid

cinnamic acid   phenyl-3-propenoic acid

ferulic acid   3-methoxy-4-hydroxyphenyl-3-propenoic acid

caffeic acid   3,4-dihydroxyphenyl-3-propenoic acid